AN INTRODUCTION TO THE PHYSICS
AND CHEMISTRY OF COLLOIDS

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BY

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PREFACE

THE present work is a slightly enlarged reprint of
a series of articles published in *The Chemical World*,
which in their turn were based on a course of ten
lectures delivered at the Sir John Cass Technical
Institute to students of very varied attainments
and interested in every branch of chemistry and of
chemical industry. The book accordingly does not
aim at a completeness precluded alike by its compass
and the extremely vigorous growth of the subject,
but is only intended to introduce readers with a
reasonable knowledge of physics and chemistry to
the fundamental facts and methods of a branch of
physical chemistry, on the importance of which it
is hardly necessary to insist.

Certain features in the selection of subjects and
in the order of presenting them, which will be apparent
to readers familiar with the existing literature, are
due to a vivid recollection of the difficulties ex-
perienced by the author in his first studies, and the
desire to spare the student as many of these as appear
avoidable. Those desirous of ampler and more
detailed information are referred to Wolfgang
Ostwald's " Grundriss der Kolloidchemie " and
H. Freundlich's " Kapillarchemie," English trans-
lations of which are urgently required.

<div align="right">EMIL HATSCHEK.</div>

LONDON,
  January, 1913.

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AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS

CHAPTER I.

THE first systematic investigation of our subject, and the name "Colloids," are due to Thomas Graham, whose results were published in a number of papers between 1861 and 1864, some of which have recently been republished and included by Wilhelm Ostwald in his series of "Classics of the exact Sciences." His discoveries may be briefly summarised under two heads. In studying dialysis, *i.e.*, the diffusion of dissolved substances through organic membranes like parchment into the pure solvent, he found that some of them passed freely through the membrane into the surrounding solvent, while a number of others failed to do so, or diffused at an extremely slow rate. Generally speaking, the former were bodies which were known to crystallise, while the latter, *e.g.*, glue, gelatine, gum-arabic, etc., were known only in the amorphous condition. Graham accordingly divided soluble bodies into two classes : Crystalloids and Colloids (from *colla*, glue).

The second discovery made by Graham, in prosecuting these researches, was that a number of

substances generally considered as insoluble could, by appropriate methods, be obtained in what at first sight appeared to be real solutions. These methods will be referred to later on, but it may be mentioned here that Graham obtained, and very carefully investigated, such solutions of silicic acid, tungstic acid, chromium, aluminium and ferric hydroxide. Most of these appeared to the eye like true solutions, *i.e.*, they were perfectly clear and apparently homogeneous. They did, however, not diffuse through parchment, and on account of this property they were called by Graham "colloidal solutions," or simply "sols," which term has now become generally accepted. These sols showed a further striking peculiarity, which distinguished them sharply from true solutions, such as, say, solutions of sodium chloride or copper sulphate, inasmuch as extremely small additions of electrolytes, and such as did not react at all with the dissolved substances, caused radical alterations in the condition of the solutions. A trace of carbon dioxide, *e.g.*, caused the silicic acid sol to set to a translucent jelly, while a small addition of sodium sulphate would precipitate the ferric hydroxide as a flocculent mass. Obviously these were phenomena quite different from known reactions of a purely chemical nature, and the sols had to be considered as systems differing from ordinary true solutions.

While Graham's investigations were the first ones directed systematically towards the production of sols and the study of their characteristic properties, numerous earlier instances of sol formation, *i.e.*, the production of apparent solutions of substances known as insoluble, are not wanting. Wöhler found in 1839 that silver citrate heated in a stream of hydrogen left a residue which dissolved in water with a red colour; this solution, which he took to be a silver subcitrate, has since been proved

to be an impure silver sol. In 1857 Faraday obtained a red liquid by reducing a very dilute solution of gold chloride with a few drops of ethereal phosphorus solution, and expressed the opinion that the gold was suspended in the liquid in a state of extremely fine distribution. In the fifties sols of silicic acid, aluminium hydroxide and ferric hydroxide were prepared respectively by Kühn, Crum and Pean de St. Gilles, and some very much earlier instances have recently been brought to light by The Svedberg, Prof. Walden, and others.

Since Graham's time the whole subject has been studied by an ever-increasing number of investigators, both physicists and chemists, with new methods and appliances, the most important of which has been the " Ultra-microscope," invented in 1905 by R. Zsigmondy and H. Siedentopf, which, even in that short time, has enormously enlarged our knowledge of colloidal solutions. The principal step forward in theory has been the proof, now quite conclusive, that " colloids," in Graham's sense, are not a definite class of substances, but that by suitable methods a very large number of bodies can be prepared in a colloidal condition, which thus presents itself as a *state*, not as *form* of matter. Thus, *e.g.*, sodium chloride is certainly a very well-defined crystalline substance; yet a colloidal solution of sodium chloride in petroleum ether has been prepared by Paal. Most of the metals have been obtained as sols, and the silver and mercury sols are made commercially and are used in medicine. Even the alkali metals have been obtained in the colloidal state by the use of organic solvents, low temperatures and experimental arrangements of great ingenuity. Similarly a large number of sols of oxides, hydroxides and sulphides are known, and especially the latter have

been used largely in several classical investigations, to which we shall have occasion to refer later on.

. All these sols are laboratory products, prepared by certain well-defined methods and with numerous precautions. They are in general very dilute, rarely containing more than fractions of one per cent., and either quite clear or slightly opalescent. Many of them, *e.g.*, the gold sols, are beautifully coloured and show pseudo-fluorescence, *i.e.*, the colour in transmitted light is different from that in reflected light. They all have one characteristic in common : on addition of varying, but always small, quantities of an electrolyte they undergo a marked and irreversible change, the solid matter being precipitated or the whole liquid setting to a jelly.

In striking contrast to these artificially prepared products there exists a large group of substances, which can be dissolved at once without special methods to form colloidal solutions, and this comprises such important organic bodies as gelatine, albumin, starch, agar, etc. These differ a good deal from one another in their behaviour. Some, like gelatine, form solutions above a certain temperature; when this falls below a limit depending on the concentration, the solution sets to a jelly, which can be " melted " again, and this can be—with certain precautions—repeated. On the other hand, egg albumin is soluble at ordinary temperatures, but on heating coagulates to a mass, which is now insoluble. Gum-arabic, to name a third substance belonging to this class, forms a viscous liquid which does not set to jelly on cooling nor coagulates on heating. Similarly varied is the behaviour of these organic substances towards electrolytes, but they all share with the inorganic sols the one characteristic property of not diffusing through a parchment membrane.

In this class, too, it is not necessary that the

solvent should be water, and a number of solutions have lately assumed very great industrial importance in which this is not the case. Thus it is very generally known that cellulose dissolves to a viscous solution in Schweizer's reagent—copper oxide-ammonia—and this cellulose sol is one of the materials used in the production of artificial silk. The solutions of nitro-cellulose in various solvents, such as ether-alcohol, acetone and acetic acid, are equally well known, and form the starting material in the production of artificial silk, photographic films, etc. Recent experiments with solutions of nitro-cellulose in acetone, which were dialysed against pure acetone, have shown that these sols also share the general characteristics of the aqueous sols, inasmuch as they do not diffuse.

In close connection with this property is another quite general feature of colloidal solutions : that they do not show any appreciable osmotic pressure, or, in other words, no raising of the boiling or lowering of the freezing point. Whether this absence of osmotic pressure is due to the large size of their molecules and high molecular weights, we shall have to discuss later in considering the theory of colloidal solutions more in detail.

One other property of colloids, which shows itself particularly strikingly in their " gels "—as Graham called the products obtained by the coagulation of sols—is their capacity for taking dissolved substances out of solution and retaining them often with very great tenacity. This phenomenon, which is of the greatest importance in nature and in many industries, is now generally called " Adsorption," and has become the subject of most extensive and careful investigation. Instances will occur at once to our readers. Specially striking is the power of " selective adsorption " (the term explains itself) possessed by many substances and organisms.

Thus we should probably be quite ignorant of the existence of one important element, iodine, and should certainly not be able to use it freely, if it were not for the selective adsorption exerted by a number of seaweeds, as iodine cannot be shown to be present in sea-water by any of the usual tests.

Before entering upon the closer study of colloidal solutions, it may be well to answer two questions, which will naturally suggest themselves to the reader who has had no practical experience of the subject : how is it possible to tell whether a given solution contains colloids ? and how can a few typical inorganic sols (the organic ones are more or less well known) be conveniently prepared ?

As regards the first question, the most direct method—apart from ultra-microscopic examination, which requires expensive apparatus and considerable expertness, and will be dealt with later—of differentiating between true and colloidal solutions is still dialysis. This may be carried out in a number of different appliances. Graham's original dialyser, which is shown in text-books and price-lists with that persistence with which certain illustrations reappear long after they have become obsolete, has the drawbacks of small surface and of being difficult to get tight. It can, however, be easily improvised, as it consists simply of a shallow open cylinder, over one end of which the parchment paper membrane is tied. The solution to be examined is then filled into this cylinder, which is placed in a larger vessel, filled to the same level with the pure solvent, generally, of course, distilled water.

A very large surface is obtained, and the tying of the membrane is avoided by the use of parchment tube—sometimes inelegantly called "sausage skin" dialysers. These can be obtained in various diameters and are inexpensive, but frequently defective. It is therefore advisable, before proceeding

to actual work, to select a piece free from defects
by hanging up a length in U-shape and filling
with distilled water. If no leak shows itself the
piece may then be emptied, hung
up again in the shape of a U
(Fig. 1) in a tall cylinder and
filled with the solution under ex-
amination. The cylinder is then
filled with the solvent, or, prefer-
ably, a constant slow circulation
is established by running the sol-
vent in continuously and syphon-
ing it off from the bottom.

For examining small quan-
tities only, by far the most con-
venient method is the use of
the diffusion shells made by
Schleicher & Schüll. These are
seamless thimbles of stout parch-
ment paper, which can be ob-
tained in several sizes.

The simplest way to use one is
to fill it with the liquid to be
dialysed, and then to place it in a
small Erlenmeyer flask filled with
water, which is changed as occasion
requires. (Fig. 2.)

In all cases the dialysis may be
considered complete when the out-
side water remains pure—which
may, of course, be tested by suit-
able reactions or conductivity
measurements. Whatever residue

FIG. 1.

is then left in the dialyser is in colloidal solution.

As regards the second query, exact instructions
for preparing a number of sols—all of them typical
—are given in the following. To avoid failures
it is absolutely essential to observe scrupulous

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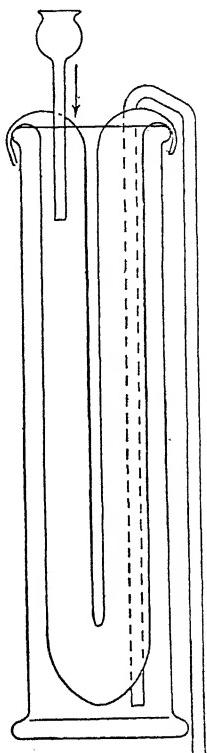
cleanliness. The water should be freshly distilled,
if necessary re-distilled with a hard glass con-
denser. All vessels used should be of Jena glass,
preferably new, but in any event cleaned with nitric
or chromic acid.

Gold solutions.—Four cc. of the commercial
1% gold chloride solution is diluted with 100 cc. of
distilled water. A solution of 2 gr. of tannin—the
" tannic acid, pure " of commerce—in 100 cc. of
water is then made up. If one part of the dilute
gold chloride solution is
mixed with three parts of
the tannin solution, a blue
gold sol results ; if equal
parts are taken, the result-
ing gold sol is ruby red.
In both cases the reaction
takes about a minute to
complete itself. These sols
are very stable and can be
kept for some time: as they
contain tannin in excess
they are, however, like pure
tannin solutions, liable to
go mouldy.
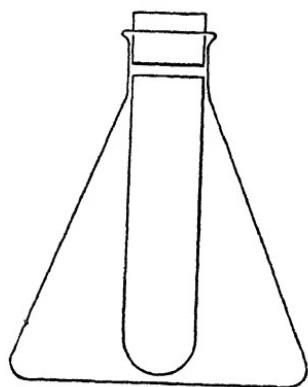
FIG. 2.

A great range of, much
less stable, sols can be obtained by using instead of
tannin one of the photographic developing agents as
reducer, *e.g.*, hydrokinone, or pyrogallol, about one
part in 500 of water. The latter occasionally gives a
fine sol, blue in transmitted and brick-red in reflected
light.

Silver sols.—These are much less stable, but
one fairly satisfactory in this respect may be
prepared in the following way:—To 5 cc. of 1 %
silver nitrate solution add, drop by drop, ammonia,
until the precipitate just disappears, and then dilute
with 100 cc. of water. If equal volumes of this

solution and of the tannin solution just described are mixed, a silver sol results, which is clear and brown in transmitted light, but often shows a greenish colour in reflected light, resembling certain petroleums.

Antimony trisulphide sol.—Dissolve 2 grammes of potassium-antimony tartrate ("tartar emetic") in 100 cc. of water. Make a dilute ammonium sulphide solution, about one part of the "strong" sulphide to 25 parts of water, and mix equal volumes of the two solutions. The colour gradually changes to yellow or orange. This sol, like the preceding ones, may then be purified by dialysis.

Arsenic trisulphide sol. — Boil 2 grammes of arsenious acid (white arsenic) for a few minutes with 150 cc. of water, then filter and allow to cool. If hydrogen sulphide is then passed through the cold solution, it gradually turns orange, with a strong greenish surface colour in reflected light.

Ferric hydroxide sol.—This sol is very easily obtained in the following manner : heat about 500 cc. of water to boiling in a beaker or Erlenmeyer flash. While it is boiling add about 5 cc. of a 33% solution of ferric chloride (which has been filtered, if necessary). The colour at once changes to a beautiful brownish-red, the sol being perfectly clear and very stable. It can be kept for weeks without any special precautions, but may be dialysed to remove the free hydrochloric acid formed by the dissociation.

These sols have been selected as being very easy to prepare and as showing all the typical qualities of colloidal solutions. Two of these may very easily be studied : the appearance with " Tyndall " illumination and the behaviour towards electrolytes. To show the former, the sol is placed in a glass vessel with plane parallel sides, and a strong beam of light—the light of a small

arc or a Nernst lamp concentrated by a lens does very well—projected through the liquid. This, if looked at from the side against a dark background, will appear turbid, with a greenish sheen in the case of the gold and silver sol.

As regards the behaviour of the sols towards electrolytes, it is only necessary to add a few drops of any salt solution—preferably barium or calcium chloride in the case of the metal and sulphide sols, and sodium sulphate for the ferric hydroxide sol—to see a marked change at once. The solutions become turbid, change colour, and after some time the dissolved substance will be found to have settled out. This may take some hours with the gold and silver sols, but if the sodium sulphate is added to the ferric hydroxide sol while the solution is still hot, the ferric hydroxide will come down as a flocculent mass in a few minutes.

CHAPTER II.

IN the preceding chapter some general characteristics of colloidal solutions, such as their appearance with suitable illumination and their behaviour on the addition of electrolytes, have been referred to, and one method of investigating them —dialysis—has been described in some detail. It now remains to describe the other methods applied to the study of colloids in more recent times, and to see what conclusions as to the nature of the colloidal state, or in other words the difference between true and colloidal solutions, can be drawn from the results obtained by these various methods.

As regards dialysis, it must be added that parchment paper is by no means the only suitable membrane for this purpose. Collodion membranes— left by the evaporation of a solution of nitro-cellulose in ether-alcohol—and fish-bladder are used extensively, especially in physiological work. The effect, however, is always the same: all these septa permit the passage of true solutions, i.e., of liquids in which the dissolved substance is present in a state of molecular or even smaller division, while they retain colloids. If we ask ourselves for the reason of this phenomenon, the simplest answer is obviously that the colloids are present as particles or aggregates too large to pass through the pores in the membranes. They may of course actually have molecules of this size: a dye-stuff, Congo Red, e.g., which lies on the border between true and colloidal solutions, contains 72 atoms, and has a molecular weight of 654, and bodies like the

albumins no doubt have molecules of still more considerable size. On the other hand, this explanation is hardly applicable to inorganic sols, especially metal sols, and it is necessary to suppose that these contain aggregates formed of a very large number of molecules.

It is, however, impossible to draw any conclusions as to absolute size from the process of dialysis, in view of its being carried out without any pressure. It is quite easy to retain particles by ordinary filtration without much pressure, which are very much smaller than the pores in the filtering material : bacteria, e.g., are retained by sand filters, although they are very much smaller than the interstices between the sand grains. To eliminate this difficulty, various investigators have attempted to retain colloids by filtration under pressure through very dense media, such as the filter candles used in bacteriological work. Amongst the earliest experiments are those by Linder and Picton with arsenious sulphide sols. These varied according to the method of preparation : most of them passed through the filter unaltered, but a portion of the sulphide from certain sols was retained. For these isolated cases a limit value of the size of the particles could thus be obtained.

Much more extensive data can be gathered by the aid of a method for separating colloids invented by H. Bechhold, and called by him, in allusion to the ultra-microscope, "Ultra-Filtration." Membranes similar in nature to those used in dialysis are employed, but these are not immersed in the solvent, and considerable pressure is used. To permit of the latter, the membranes are prepared in the following manner : strong hard filter paper is impregnated, generally in vacuo, with either a gelatine solution or acetic acid collodion of known strength. The gelatine filters are then rendered

insoluble by immersion in cold formaldehyde for several days, while the collodion filters are immersed in water, which gradually dissolves the acetic acid and leaves a gelatinous mass of nitrocellulose in the substance of the paper. The filters are clamped in a small pressure vessel and are supported on wire gauze and perforated metal, so that pressures up to ten atmospheres can be used. A very important feature, predicted and subsequently verified by Bechhold, is the ease with which the porosity of these ultra-filters can be varied by altering the strength of the original gelatine or collodion, so that colloids which passed freely through a " $2\frac{1}{2}\%$ " collodion filter, *i.e.*, one made from a collodion containing $2\frac{1}{2}\%$ of nitro-cellulose, could be entirely retained by one made from 5% collodion.

The size of the pores in these filters can be determined by two methods proposed by Bechhold and by a third one suggested by the author and also tried by Bechhold. They are all based on various properties of capillaries and need not be discussed here in detail. According to the concentration of the collodion or gelatine the diameters of the pores lie between 930 $\mu\mu$ and 21 $\mu\mu$. (The $\mu\mu$, which is the unit generally employed in giving the dimensions of such particles as we shall have to deal with, is 0·001 μ, while the μ, which is generally employed in ordinary microscopic measurements, is 0·001 mm. The $\mu\mu$ is therefore one millionth millimetre.) These dimensions give us limits for the sizes of the particles retained by such filters : if the particles are retained, they are probably, though not necessarily, larger than the pores; if they pass through the filter, it is reasonably certain that they are much smaller than the pores.

Evidence tending in the same direction and towards the same limits is afforded by an optical property of the sols to which reference has already

been made : their turbid appearance in the Tyndall cone. If such a cone is produced, *e.g.*, in a gold sol, it appears greenish, and if this greenish reflected light is examined by a suitably placed analyser, it is found to be polarized. It may be worth mentioning that herein lies its difference from true fluorescence : the blue light, which under similar conditions appears in a solution of quinine sulphate, is not polarised. The whole phenomenon has been mathematically investigated by Lord Rayleigh, and it has been proved that, to produce it, the particles reflecting the light must be small compared with the wave length of light. The values of the latter are of course known accurately and lie between 450 and 760 $\mu\mu$ for the visible spectrum. These limits again agree very well with those deduced from the experiments with ultra-filters.

At the same time they answer a question which may already have occurred to the reader : why the size of such particles as may be present in a sol cannot be determined directly by microscopic observation and measurement ? The answer is that particles, which are small in comparison with the wave length of light, are invisible in the ordinary microscope. It was shown by Abbe in his classical investigations on the microscope that the lower limit of visibility varied from 0·8 to 0·4 μ, *i.e.*, 800 to 400 $\mu\mu$. As a matter of experience, all sols which appear clear to the eye, and many which appear distinctly turbid, entirely fail to show any particles with the ordinary methods of illumination.

It has, however, been known for some time that with favourably arranged illumination objects of sub-microscopic dimensions could be rendered visible. Thus it had been shown by Fizeau and Ambronn that slits of much smaller width than the lower limit of visibility could be seen if they were

strongly illuminated in a dark field. This observation suggested to Zsigmondy and Siedentopf the possibility of rendering visible the individual particles which collectively produce the Tyndall phenomenon, if only the light reflected or dispersed by the particles was permitted to enter the instrument, but no direct rays from the source of light.

This expectation has been brilliantly realised and the "Ultra-microscope"—as the microscope fitted with this peculiar form of illumination has
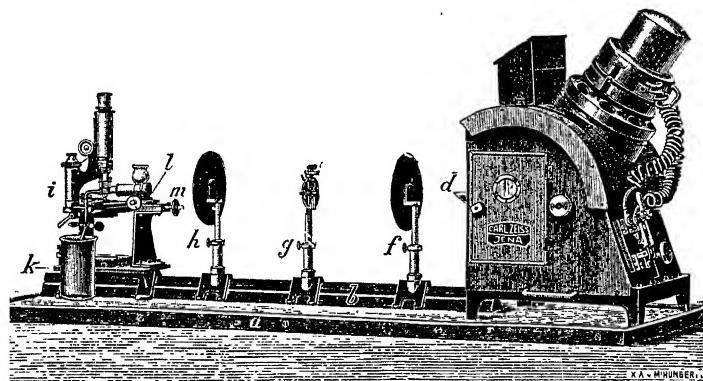
FIG. 3.—GENERAL ARRANGEMENT OF THE SLIT ULTRA-MICROSCOPE.

been called—has now become an indispensable instrument of research. The principle of it is very simple : a powerful beam of light is thrown horizontally through a small body of the liquid, which is observed through a microscope, the axis of which is vertical. It is at once obvious that no light can enter the instrument, except such as has been reflected or dispersed by particles present in, and optically different from, the liquid itself, i.e., they must either be opaque or possess a refractive index different from that of the latter.

The details of the actual arrangement, which have called for the exercise of very great ingenuity, are shown in Fig. 3. The light of the arc lamp d is projected by the lens f on a "precision" slit g,
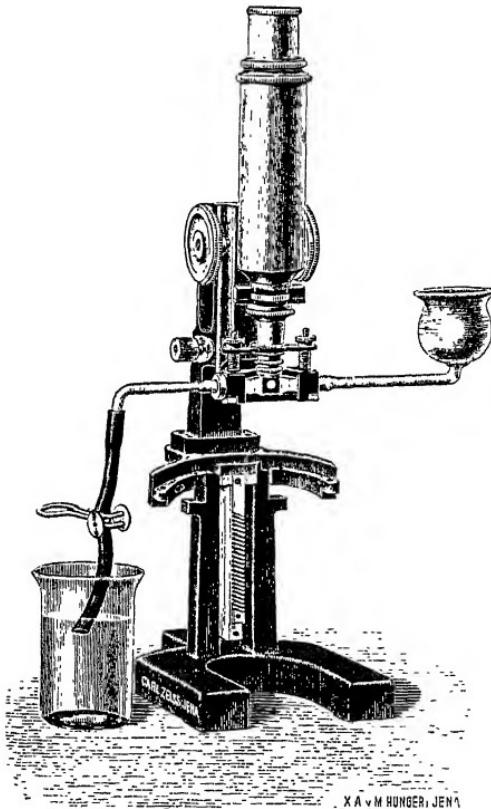
FIG. 4.—MICROSCOPE WITH QUARTZ CHAMBER FOR ULTRA-MICROSCOPIC EXAMINATION OF LIQUIDS.

the width and height of which can be adjusted very accurately. An image of the slit is formed by the second lens h and projected on the illuminating device proper, l, which is substantially a microscopic objective. This throws a narrow and intense

beam of light through a cell containing the liquid, which is seen more distinctly in Fig. 4. It is of rectangular section and has two windows—the one in front admits the beam of light, while the second one is at the top and opposite the objective of the microscope. The cell is provided with a funnel at one end, and an outlet at the other, so that a large volume of liquid can be passed through the cell and examined in one setting.

As already explained, no light enters the microscope except such as is reflected from particles in the liquid, and the image formed bears no relation to the actual size of the former, but depends on the intensity of the illumination and the qualities of the microscope only. Direct measurement of the particles is therefore still impossible, but indirectly the diameters may, with certain assumptions, be determined by calculation in the following manner : The width and depth of the illuminated prism of liquid is measured by means of an eye piece micrometer, and the number of particles in the volume thus determined is counted. If the content of the sol—say the amount of gold in a gold sol—is known, the weight of gold in the illuminated volume is also known, and from this and the number of particles the weight of a particle can be calculated. Assuming the particles to be a simple geometric shape—say spherical or cubical—and their density to be that of solid gold, the diameter or edge can again be easily calculated.

In this manner the sizes of the particles in many sols, especially of the metals, have been calculated, and these agree within reasonable limits with values obtained by Bechhold from experiments with ultra-filters.

With direct sunlight particles of 5 $\mu\mu$ dia. can still be seen. In many sols, however, particularly organic ones, no particles can be

seen even in those circumstances, but only a diffuse light. This may be due either to their small size, or else their having a refractive index very near that of the liquid. Particles visible in the microscope are generally described as microns; those which can be made visible by the ultra-microscope as submicrons, and those which cannot be resolved even by the latter method as amicrons.

The apparatus just described is the most perfect one for the observation of ultra-microscopic particles, and the only one which permits measurements to be made. As it is rather costly and requires very powerful illumination, a number of simpler devices have been introduced, in which the light is projected through the film of liquid parallel with the axis of the microscope, but certain arrangements are made to prevent direct light from entering the instrument. The principle of all these
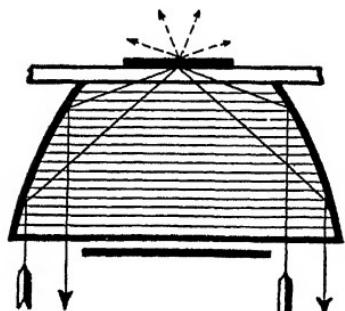
FIG. 5.—SECTION OF PARABOLOID CONDENSER, SHOWING PATH OF RAYS.

appliances is the same, and will be readily understood by reference to Fig. 5, which shows a section of the "paraboloid condenser" made by Carl Zeiss. The condenser is a paraboloid of revolution, of glass or rock crystal, bounded by two parallel planes. Parallel rays entering the condenser are, as is well known, reflected into the focus of the parabola, and the top of the condenser is so adjusted that this focus falls on the surface of the slide, which is of a definite thickness. A central stop covers the bottom of the paraboloid, and permits only such rays to pass as will, after reflection, strike the surface under an angle greater than the critical angle, so that they would

be totally reflected by the top of the condenser, if
in contact with air. By placing water or cedar oil
between this surface and the slide the light is enabled
to pass through the slide and any liquid placed on it,
but is totally reflected at the cover glass placed on
the liquid. If, however, the latter contains particles,
light is dispersed from them—as indicated by the
dotted lines—which can enter the microscope and
form an image.

This and similar condensers can be fitted to any
microscope, and can be used for rendering visible
submicrons, a Nernst lamp or incandescent gas
mantle being quite sufficient for illumination.
Measurements are not possible, as the volume of
liquid cannot be accurately determined.

From the foregoing it appears that colloidal
solutions in many cases contain particles which can
be made visible by appropriate means, and whose
size can be determined. The sizes are still very
considerably larger than the limit values for the size
of various molecules arrived at by numerous in-
vestigators employing a great variety of methods.

In this presence of particles of sizes greatly ex-
ceeding molecular dimensions, must be sought one
of the fundamental differences between colloidal
and true solution. To emphasise this, we shall in
future employ the terminology now in general use,
by calling the colloidally dissolved substance the
"disperse" and the solvent the "continuous"
phase, terms which explain themselves and form
a constant reminder of the fact, that colloidal
solutions are systems of two phases.

A knowledge of these sizes, however, does not,
by itself, explain the striking differences between
various types of colloids, nor does it form a basis
of classification. These differences are particularly
marked as regards the behaviour towards electro-
lytes, which precipitate one type—the inorganic

sols—even in small quantities, while they have little effect on many organic colloids—such as gelatine, agar, etc.—even in large quantities. A division into " lyophobic " and " lyophilic " colloids—*i.e.*, such as remain reluctantly and such as remain freely in solution—has been based on this difference by Perrin and Freundlich. This is, however, merely descriptive, and the classification adopted by Wolfgang Ostwald appears for many reasons preferable. This takes for its basis the consideration that the disperse phase of a sol may consist of either liquid or solid particles, and explains very many of the differences between the two principal types of colloids on this basis. It is only natural that a variety of factors are necessary to make the reasoning which underlies this classification convincing. Some of these will be considered later on, and for the moment we will confine ourselves to studying in some detail one physical property which, even if taken by itself, makes some such assumption as that quoted above necessary, that is the viscosity of various types of sols.

CHAPTER III.

THE reader is no doubt aware of what is under-
stood, in a general way, by the viscosity of a
liquid : the resistance offered to shearing, stirring
or the flow through a capillary tube. If a liquid is
contained between two parallel plates and one of
these is moved with a constant velocity in its own
plane, a certain force is required, which depends on
the velocity, the surface and distance of the two
plates, and of course on the nature and temperature
of the liquid. This gives us the definition of the
" viscosity coefficient" at any temperature : the force
required to move a plate of unit surface separated
from another plate of the same size by a layer of
liquid of unit thickness, at unit velocity. Such
coefficients for many liquids, expressed in gramme-
centimetre-second units, can be found in Landolt
and Börnstein's tables.

As regards colloidal solutions, they divide them-
selves into two classes, if the increase of viscosity,
compared with that of the solvent or continuous
phase, is taken as the basis of classification. One
class, the metal and sulphide sols in particular,
shows a viscosity only very slightly higher than
that of water. The other, which comprises prin-
cipally the organic colloids, such as albumin,
gelatine, gum arabic, agar, etc., shows a very
marked increase of viscosity, even if the percentage
of dissolved matter is small. To explain this
difference some of the earlier investigators in this
field, more especially Quincke, resorted to reason-
ing by analogy, based on the known behaviour of

systems containing the disperse phase in a much coarser form than do the sols. It is a fact familiar, to everybody who has stirred up finely divided solid matter, such as a precipitate of calcium carbonate or barium sulphate, with water, that even 20 or 30 % do not offer a very great resistance to stirring, *i.e.*, do not cause a great increase of viscosity. On the other hand, it is equally well known that systems of two liquids insoluble in each other, generally called emulsions, can under certain circumstances show enormous increase in viscosity compared with either phase. Various pharmaceutical preparations coming under this head are familiar to everyone; extreme cases are represented by some emulsions used as lubricants, and by Pickering's emulsions with 99% of oil in 1% of soap solution, which could be cut into cubes.

Applying these considerations to sols, we are led to the conclusion—now generally accepted— that in those which show a low viscosity the disperse phase is present as solid particles, while in the sols with high viscosity the disperse phase is liquid. An albumin sol, for instance, would consist of a dilute solution of albumin, in which are dispersed drops or globules consisting of a much more concentrated solution. This conception is certainly not an easy one, and will receive further discussion when we arrive at the detailed consideration of the class of colloids to which it applies, but it is the only one which explains all their peculiarities. Nor does it rest only on the analogies set forth, but is strongly supported by mathematical investigations, undertaken independently and by entirely different methods, by A. Einstein and by the author during recent years. These show, that the presence of *solid* particles in a liquid can only raise the viscosity by small amounts simply proportional to the volume of

solid matter present; when a few per cent. of—apparently—solid matter like agar raise the viscosity some hundred times, it follows that the disperse phase cannot be solid.

Systems consisting of solid particles of microscopic size distributed through a liquid are generally called suspensions, while those having two liquid phases are called emulsions. Wolfgang Ostwald accordingly calls the sols resembling the former "Suspensoids," and the sols which resemble the latter, in showing markedly high viscosities, "Emulsoids," which terminology we shall adopt in future. These two classes coincide to a very great extent with the "lyophobic" and "lyophilic" colloids.

The suspensoids show a much more uniform behaviour towards various influences than the emulsoids, and will, therefore, be considered first. We are now in the possession of two distinct data : we know the approximate size of the particles in a large number of sols, and we have concluded that they are solid. The next step is to co-ordinate these two factors by examining the behaviour of small particles suspended in a liquid, and especially how this changes when their size decreases to ultra-microscopic dimensions.

It was shown by Stokes in 1850 that a *small* sphere falling in a liquid soon assumes a constant velocity, which is given by a formula that has been used in an enormous number of most important investigations, and has led to numerous results of great value. If we call

r the radius of the particle,
s the specific gravity of the same,
s' the specific gravity of the liquid,
η the viscosity coefficient of the latter,
g the gravity constant,

the constant velocity of the particle is :—

$$V = \frac{2r^2\,(s-s')g.}{9\eta}$$

It is obvious that the difference (s—s') may be positive, zero or negative, that is the particle may sink, remain stationary or rise if its specific gravity is greater, equal to, or smaller than that of the liquid. It is also obvious that the velocity, in whichever direction, is inversely proportional to the viscosity of the liquid : a particle of a given size and weight will sink several hundred times faster in water than in castor oil. The point which, in the present connection, interests us most is, that the velocity is—other things being equal—proportional to the square of the radius.

To fix ideas it will be useful to consider an example in figures, say a gold particle of 1 μ radius or 2 μ diameter. Introducing the proper values (all in cm., gr. and seconds), *viz.*, $r = 10^{-4}$, $s = 19\cdot3$, s' (water) = 1, g = 980, η at 20° = 0·01, we find the velocity of the particle about *0·04 mm.* per second, or 2·4 mm. per minute.

This is, of course, a considerable speed, and means, in other words, that such a suspension of gold particles would clear at the rate of 2·4 mm. per min. from the top, and would be clear to a depth of about 14 cm. after one hour.

Assuming now the radius to be 1/100 of that just considered, or 10 $\mu\mu$, which is the size of the particles in a red gold sol as determined by many measurements, the velocity would be 1/10,000 of that calculated. This makes it only *0·0144 mm.* per hour, or about 10 mm. in one month. With particles of lower specific gravity the rate of settling would, of course, be still lower, *e.g.*, with a sp. gr. of 3 it would be a little over *one mm.* per month.

This little calculation shows us, that with particles sufficiently small and not much heavier than the liquid, a suspension may appear very stable and take a very long time to show any marked clearing. At the same time, we already are familiar with one property of sols—their liability to undergo irreversible transformation—which precludes our accepting mere smallness of particles as a sufficient explanation of the stability of many sols. A suspension is reversible: when it has settled, however long the process may take, it can be shaken up again, and this may be repeated indefinitely. This is not possible with a sol like the metallic sols; when this has coagulated, the gel cannot by mere shaking be transformed back into the original sol. We are therefore forced to the conclusion that the particles are subject to other influences besides those of gravity and viscosity. Investigation has shown this reasoning to be correct, inasmuch as the particles are in violent motion, and are also electrically charged.

The motion of the particles in a sol is the most striking feature in the ultra-microscopic image. It is, however, visible even with much larger particles and ordinary illumination, and was first observed as far back as 1827 by Dr. Brown, a botanist, after whom it is called the Brownian movement.

The movement is composed of an oscillating motion of the particles round a central position, and an erratic translatory motion. Description is rather inadequate, but the movement can be seen very well in a suspension of gamboge (the ordinary water colour) with magnifications of about 500 diameters and such simple dark ground illumination as can be obtained with a central stop in the ordinary condenser.

It was soon found that the motion decreased as the particles grew larger, and did not show itself at all if the diameter exceeded a certain size. Various

suggested causes, such as vibration, convection currents due to changes of temperature or of concentration were gradually eliminated by experiment, and it became evident that the movement could hardly be due to any transient cause when it was found that small gas bubbles in liquid enclosed in crystals still showed it. The opinion gained ground that the origin of the movement had to be looked for in some factor inherent in the liquid state. The study of the phenomenon received an enormous impetus by the invention of the ultra-microscope, as the very small particles disclosed by it for the first time showed it so vividly that Zsigmondy was inclined to look on it as something differing not only in degree but also in kind from the Brownian movement as known up to then. Methods were devised which facilitated the measurement of the amplitude of oscillation : Svedberg allowed the liquid to flow through the field, while Siedentopf photographed it on a falling plate. In both cases the oscillating motion of the particle is combined with the rectilinear motion of the liquid or the plate, so that the images seen directly in the first, and photographed in the second method, appear as wave lines, which permit convenient measurement of the amplitude and of the period, *i.e.*, the time between two similar positions. Svedberg found the first two mathematical relations between these quantities : the amplitude is directly proportional (for particles of one size) to the period, and inversely proportional to the viscosity of the liquid.

In 1906 the phenomenon was treated mathematically, by entirely different methods, by Einstein and by v. Smoluchowski, on the definite assumption that it was due to the impacts of the molecules of the liquid on the particle. The two physicists arrived at formulæ identical except for a numerical constant, and showing that the motion was determined only by the constants of the liquid, *i.e.*, temperature and

viscosity, and by the diameter of the particles, but was independent of the mass of the latter. They also confirm Svedberg's results. In a further investigation, involving experimental methods of extreme ingenuity, Perrin showed that the whole phenomenon conformed to conclusions drawn from the kinetic theory, and that there was no essential difference between these particles and molecules; that, in other words, they could be treated as molecules of a substance with extremely high molecular weight : of the order of 1000 millions in the case of the mastic particles used by him. Perrin's paper has been translated into English by Soddy and the reader is referred to this work for full details.

It follows from Perrin's investigation that particles in Brownian movement—like molecules of a gas or a dissolved substance—tend to fill the space in which they are contained according to definite laws. The movement must therefore be considered as one of the factors which keep a sol stable, but is not, by itself, sufficient to account for its stability, as particles showing moderate Brownian movement may still settle with comparative rapidity. The stability is intimately connected with the electric charge, to which reference has already been made. It may be said generally that any substance in contact with water and many other liquids, assumes an electric charge, the origin of which is not definitely explained. Most substances become negatively charged in contact with water : the charge can be varied and even reversed by the addition of electrolytes, and may become zero at suitable concentrations. In this condition, as shown by Burton and by Hardy, sols are particularly unstable, and tend to precipitate.

It need hardly be mentioned that the electric charge is not confined to submicroscopic particles, but is found equally on the particles of a coarse suspension. It has also been known for a considerable time that

the speed of settling in many suspensions—which settle in any event—can be increased by the addition
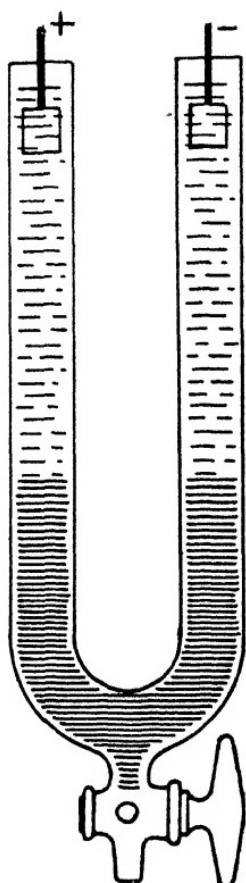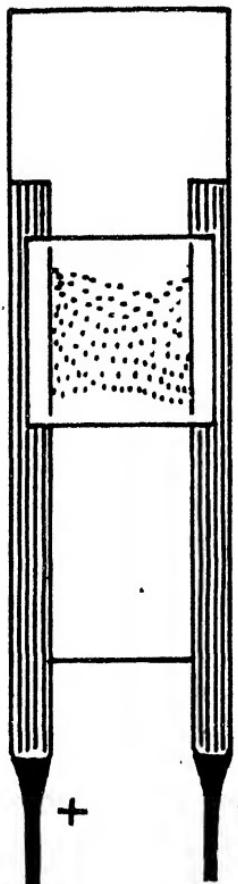
FIG. 6.   FIG. 7.

of electrolytes. The greater sensitiveness of the highly dispersed systems must be ascribed to the very much greater charge due to the enormous increase in surface. At the same time, while the

existence and the stabilising influence of the charge is
fully established, it must be said that the origin of
the charge and the mechanism of its action is still
rather obscure.

Before we proceed to study suspensoids in de-
tail, it may be worth mentioning how the electric
charge on the particles can be demonstrated. This
can be done, for instance, by placing the sol to be
examined into the bend of a U-tube (Fig. 6) and
filling the limbs with pure water, into which dip
electrodes connected to some source of current.
The particles gradually wander into the water sur-
rounding the pole of opposite sign, so that nega-
tively charged particles wander to the anode.

Another very convenient method, permitting the
use of small volumes of liquid is the microscopic
method, as used first by Cotton and Mouton. An
ordinary microscope slide (Fig. 7) is provided with
a pair of electrodes of platinum foil, which are con-
nected by suitable leads to a couple of cells or
accumulators. A drop of the liquid under examina-
tion is placed on the slide so as to touch both elec-
trodes and covered with a cover glass. The
preparation is examined under the microscope—
using one of the ultra-condensers described in the
previous chapter, if necessary—and the particles
are seen to travel to the anode, if negatively, or the
cathode, if positively charged.

Both the U-tube and the microscopic method
also permit the actual charge on a particle to be
measured, by observing the rate of travel and the
strength of the electric field, i.e., the difference in
voltage divided by the distance of the electrodes.
We need only mention here that a very large
number of different materials have been so ex-
amined, and that the charge carried by a particle
is very much the same in all cases.

CHAPTER IV.

In the preceding chapter we have fully characterised the suspensoids as systems containing the disperse phase as solid particles below a certain size, in constant movement and electrically charged. A few typical suspensoids—the gold, silver, antimony and arsenic sulphide sols—have already been referred to in the first chapter, where directions are given for preparing them.

These directions have one feature in common : the metal is reduced or the sulphide produced by a suitable reaction in very dilute solution. This procedure is applicable in many cases, though not universally, and sols of silver, copper, mercury, platinum, palladium, etc., have been prepared by reducing very dilute solutions of their salts with a great variety of reducing agents, such as hydrogen, hydrazine and hydroxylamine compounds, acrolein, hypophosphorous acid, and many others. Many sulphides and haloid compounds can also be obtained in a similar fashion. The reason why all these processes can be carried out in very dilute solutions only is clear : we already know that the suspensoid sols are precipitated by varying, but always small, amounts of electrolytes. As practically all the reactions mentioned lead to the formation, not only of the disperse phase which it is desired to obtain, but also of electrolytes, it is obvious that the concentration of these must be kept below a certain limit, or, in other words, that it is necessary to work with very dilute solutions.

A number of other methods have been applied

with considerable success, several of which may be classed together as " disintegration methods." The most important of these is that of Bredig, first published in 1898, which consists in producing a small electric arc between electrodes made of the metal which is to be dispersed, under water. With suitably proportioned electrodes, current strengths, and cooled liquid, sols of many metals can be prepared, including platinum, iridium, palladium, gold, silver, copper, lead and others. The method has been considerably developed and improved by Svedberg, who substituted for the arc an oscillating discharge between electrodes of aluminium or zinc (which resist disruption) between which the metal to be dispersed is suspended as foil. He also used, instead of water, a number of organic compounds, such as ether, pentane, isobutylalcohol, etc., and, by cooling with liquid air, was able to prepare sols of the alkali metals, barium, strontium, and many others. An interesting feature of many of these sols is their colour, which in most cases is the same as that of the vapour.

Another disintegration method, invented by Kuzel, and applied particularly to the metals of the bismuth and chromium groups, consists in grinding the material as fine as possible in ball mills and then treating it repeatedly and for many days alternately with strong alkali and acid. When these are finally replaced by water, the metal is found to be reduced to so fine a state that it forms a sol.

In a few cases no treatment at all is required, but the metal goes directly into colloidal solution on contact with water, or at least on boiling. Lead, *e.g.*, has been shown by Mme. Traube-Mengarini and A. Scala to form a sol at once on contact with distilled water : if, however, no precautions are taken to exclude oxygen, the dissolved lead is promptly transformed into hydroxide. The same

investigators showed that a silver sol could also be obtained by boiling distilled water for some time in silver vessels; that copper sols are formed under the same conditions, has been known for some time.

A third procedure is that called by Graham "peptisation," in allusion to the transformation of insoluble into soluble compounds by digestion. An example will best illustrate the characteristic feature of this method, for instance, the production of a cadmium sulphide sol. The sulphide is precipitated from an ammoniacal solution of cadmium sulphate, washed and finally suspended in distilled water. If hydrogen sulphide is now passed through the water, the suspension gradually becomes milky and finally perfectly clear golden yellow with a slight red surface colour. The dissolved gas may be displaced by nitrogen, or removed by boiling, the sol being extremely stable.

Of all the striking properties of the suspensoid sols, their instability in the presence of electrolytes is probably the most striking, and has received a very large amount of attention and study, particularly from English investigators—Linder and Picton, Hardy, Burton, and others. To summarise their results, at the same time excluding matter which goes much beyond the scope of this work, and is in part still highly controversial, it may be said that the first step in the coagulation of suspensoids is the neutralisation of their electric charges by that of the oppositely charged ions of the electrolyte. As most suspensoids are negatively charged, the active ion is accordingly the positive, or cation, of the electrolyte. Each electrolyte has to be present in a definite concentration to produce coagulation, and a very large number of investigations have been directed to ascertaining these minimum concentrations for various sols, and

a large range of electrolytes. The subjoined table gives the results of one of the most extensive series by Freundlich. The sol was an $As_2 S_3$ sol, containing 7·539 millimoles (*i.e.*, 1·854 grammes) of the negatively charged sulphide per litre; the electrolyte concentrations are given in millimoles per litre :—

K Cl	49.5	Mg Cl₂	0.717	Al Cl₃	0.093
KNO₃	50.0	Ca Cl₂	0.649	Al(NO₃)₃	0.095
NaCl	51.0	Ba Cl₂	0.691		
LiCl	58.4	Ba(NO₃)₂	0.687		
H Cl	30.8				

The first column contains the electrolytes with monovalent, the second those with divalent, and the third those with trivalent cations. It will at once be noticed that—in each column—the quantity of electrolyte depends only on the cation : practically the same molar concentration of potassium chloride and nitrate, barium chloride and nitrate, and aluminium chloride and nitrate produces the same effect, which therefore in each case depends only on the amount of $K\cdot$, $Ba\cdot\cdot$ and $Al\cdot\cdot\cdot$ present. A very striking difference, however, shows itself between salts containing cations of different valency, that is between the three columns of the table. The concentration of the monovalent cations is roughly 70-80 times greater than that of the divalent, and 600 times greater than that of the trivalent cation. This phenomenon, which Hardy was the first to study, is probably best explained by the theory propounded by Freundlich, to which we shall have occasion to refer when considering adsorption.

An equally important point in this connection —the comparative behaviour of ions of different valency—was first investigated by Linder and Picton. When the electrolyte is added to the sol, the particles are discharged and, as they no longer

repel one another, are free to approach and to form larger aggregates, which settle more or less rapidly. These precipitates always contain some of the precipitating cation, and investigation shows that the amounts of different cations found are equivalent. This fact—which is somewhat surprising in view of the great difference in concentration —becomes intelligible at once when we remember that equivalent quantities of all ions carry the same charge, and are therefore able to neutralize the same amount of oppositely charged suspensoid particles.

We have so far referred exclusively to sols containing only the disperse phase and the small amount of electrolytes produced by the reaction which gives rise to the formation of the disperse phase. Many reactions, however, for instance, that between lead compounds and chromates, or barium salts and sulphates, never lead to sol formation, even if carried out in very great dilution in pure aqueous solutions. In other cases such reactions do produce sols, which, however, are very unstable. It has been known for some time that the addition of very small amounts of colloids belonging to the second or "emulsoid" groups greatly increased the stability of sols: Faraday observed, that the gold sol which he obtained by reducing gold chloride solution with a solution of phosphorus in ether could be kept unaltered much longer if "a little jelly" was added to it. Similarly, if the colloid is added beforehand to one of the reacting solutions, insoluble precipitates can be obtained in so fine a state of dispersion that they form sols: thus a small addition of casein makes it possible to obtain sols of lead chromate, barium sulphate, etc. The sols so obtained also require very much larger amounts of electrolytes for precipitation than do suspensoids without such addi-

tions, which are accordingly in this connection described as "protective colloids." They all belong to the emulsoids, of which we already know that they are much less sensitive to electrolytes than the suspensoids, and their action in protecting the latter is probably best explained by Bechhold's assumption that each particle of the suspensoid surrounds itself with a layer of the emulsoid and then possesses the electrical properties of the latter.

Although many readily available substances, such as gelatine, albumin, casein, isinglass, etc., can be used as protective colloids, one group of compounds has acquired great prominence during the last few years. These are certain products of the hydrolysis of albumin by alkalies, first described by Paal and his collaborators as "protalbinic" and "lysalbinic" acids, and used by them in the preparation of a very large number of different metal sols. These show very great stability, and the silver and mercury sols, for instance, can be evaporated to dryness and then readily re-dissolved in water.

The "protective" effect of different emulsoids varies between very wide limits, and may perhaps offer one of the most delicate means for their differentiation. It has been studied systematically by Zsigmondy, who determined the quantity of colloid just necessary to protect a definite volume of a standard gold sol from coagulation by a given quantity of sodium chloride. The relative figures vary from 0·005 for gelatine, 0·02 for isinglass, and 0·2 for egg albumin, to 12 for dextrine and 25 for potato starch. They are usually referred to as the "gold values" or "gold figures" of the colloids.

CHAPTER V.

In the last two chapters we have considered systems in which the disperse phase—whether of microscopic or ultra-microscopic dimensions—consists of solid or, more correctly, rigid particles, and we now proceed to the study of systems of two liquid phases. These present several very striking peculiarities which can only be properly explained by observing either natural or artificial "emulsions," *i.e.*, fairly coarse dispersions of one liquid in another, with which it is not miscible. Both natural and artificial systems of this kind are numerous and important: of the former we may mention milk, which is an emulsion of fat globules in a solution of caseinogen, albumin, lactose and salts, and rubber latex, in which the continuous phase is also a solution of proteids, while the disperse phase consists of rubber and resin globules in varying proportions. As regards the artificial emulsions, some of them are unwelcome by-products of various industrial processes, such as the condense water from steam engines which contains a portion of the oil used for cylinder lubrication in a state of very fine and persistent division, or wool washings, in which some of the wool fat is emulsified by the action of the soaps formed from a portion of the fat. A large number of emulsions are also prepared purposely, such as a number of well-known pharmaceutical preparations, lubricating compounds, etc.

The simplest systems of this class are the pure "oil-water" emulsions, which, as the name says,

contain no soaps, proteids or other emulsifying
agents. The type of these is condense water, with
about one part of oil in ten thousand or more of
water; very similar emulsions may be obtained by
pouring an alcohol or acetone solution of an oil
into water, when the oil separates in the form of
very minute globules. In this way it is possible to
obtain stable emulsions containing up to one-
thousandth part of oil. This great dilution is quite
in keeping with what we know already about the
suspensoids, and investigation of such oil-water
emulsions, which has been carried out during the
last few years by Lewis, Ellis and Goodwin, and
the author, shows that they do not differ materially
from systems with solid particles. The oil globules
show active Brownian movement, are coagulated
by electrolytes and can even—as was first shown
by the author—be retained by certain filtering
media, for instance by the ultra-filters mentioned in
a previous chapter. This possibility proves that
very small liquid particles approaching ultra-micro-
scopic dimensions possess a high degree of rigidity,
a conclusion fully borne out by mathematical in-
vestigations carried out by the author.

While, therefore, systems of two liquid phases
containing only a small percentage of widely sepa-
rated particles differ in no material respect from
similar systems with rigid particles, a very important
difference appears as the percentage of disperse
phase increases. With rigid particles this per-
centage is obviously limited by simple geometrical
considerations. If we imagine the particles to be
spheres of equal diameter and to be so numerous
that they are in closest contact—in which case each
sphere touches twelve others—they occupy about
74% of the total volume. Such an arrangement
of *solid* particles will, however, no longer have the
properties of a liquid, but will be a mud or paste;

filter press cakes of, *e.g.*, calcium carbonate, which still contain about 40% of water, or only 60% instead of 74% of solid matter, certainly no longer resemble a liquid. If the disperse phase is liquid, that is, still easily deformed, it is obvious that the whole system will still retain the character of a liquid, even if the disperse phase occupies, or, indeed, exceeds 74% of the total volume. The globules will touch one another when the former figure is reached, and as it is exceeded will become flattened at the points of contact, developing the twelve faces of a dode-cahedron. There is thus no limit to the ratio: volume of disperse phase/total volume, which may approach unity. As a matter of fact, emulsions containing 99% of oil in 1% of soap solution have been made by Pickering.

It is quite impossible to prepare emulsions con-taining such percentages of disperse phase (or any-thing more than fractions of a per cent.) unless the continuous phase is a solution of certain substances, such as soap, various products of the saponification of albumin, or one of the saponins. All these solu-tions have one characteristic in common : they froth strongly even in great dilutions. Frothing, which never occurs with pure liquids, is a definite indication that the dissolved substance lowers the surface tension of the solvent, and the process of emulsification is closely connected with this lower-ing of surface tension, or more correctly the inter-facial tension between the two phases. This con-nection can be very easily demonstrated by an apparatus devised by Donnan, and illustrated in Fig. 8. A pipette A is provided with a length of capillary tube B, which leads into a bend C. The latter is drawn out into a point D, which is ground off flat. The pipette is filled with the oil to be examined, and the outlet submerged in the liquid which is to be the disperse phase. The size of the

drop which issues from the point D is settled on
one hand by the difference in specific gravity of the
two liquids, and on the other by the surface tension
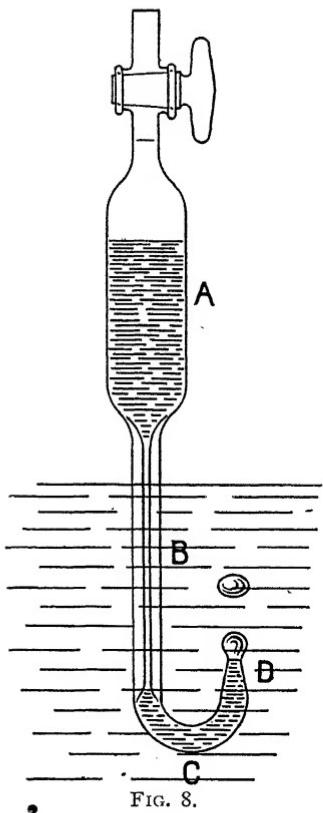
FIG. 8.

acting round the circumference of the point, which
tends to retain the drop. Any decrease in surface
tension accordingly shows itself in diminished size,
or increased number of drops, and this increase,
and the obvious parallelism between it and the

emulsifying power of the liquid, is very striking. While, for instance, a pipette used by the author gave 65 drops of light petroleum in water, it gave about 260 drops in a 1% soap solution. With such a soap solution it is quite easy to make emulsions containing over 90% of petroleum as disperse phase, and this percentage may be increased still further by certain methods indicated by Pickering.

We can now form a picture of the various factors which make possible the existence of these high percentage emulsions, and which give them their characteristic properties. The oil globules are no longer spherical, but polyhedral, the adjoining faces being separated by very thin films of the disperse phase. Such films would tear, if they had the high surface tension of water, and can only persist if the interfacial tension, which tends to tear them, is very greatly lowered by certain dissolved substances. If the films are thick, *i.e.*, if the particles are widely separated, a persistent emulsion is possible, as we have seen above, even in water. We also realise that such a system consisting of polyhedra of oil separated by thin films of an aqueous medium—or, put in the other way, a honeycomb-like structure of the latter filled with oil —must have the high viscosity which is so characteristic of the emulsions with a large percentage of disperse phase. If such liquids are sheared, the polyhedra will constantly have to slide over one another, and in the process will be stretched and deformed. In other words, the total surface of the system will be enlarged and, notwithstanding the low surface tension, a considerable amount of surface energy developed, which appears disguised as viscosity. Extreme cases are presented by some of Pickering's emulsions with 99% of oil, the viscosity of which is so great that they can be cut into cubes and retain their shape.

The stability of emulsions made with one of the emulsifying agents mentioned above varies considerably. Generally speaking, they are destroyed by the addition of all substances which affect the latter : thus emulsions made with soap solution are at once destroyed by the addition of small amounts of acid, which decompose the soap. Rubber latex is coagulated by such substances as coagulate the particular proteids which it contains, for instance, acetic acid in the case of Hevea latex. The phases can often be separated without the use of chemical agents, by centrifuging, as in the case of milk. Finally, as the globules are—generally negatively—charged, they travel in the electric field, and this method has at least been suggested for industrial application.

The actual methods of making emulsions—suitable qualities of the phases being assumed—deserve only passing mention. The two components are shaken up together until the disperse phase is sufficiently finely distributed, or the " oil " is injected into the other liquid from a syringe with a fine nozzle. Temperature naturally plays a considerable part in these operations, as it reduces the interfacial tension between the phases, and also their viscosities.

We now proceed to the consideration of the second—and by far the more important—class of colloids, the emulsoids. The only inorganic emulsoid of much importance is silicic acid, which was very exhaustively studied by Graham. If a solution of sodium silicate (" waterglass ") is decomposed by a slight excess of hydrochloric acid, and the mixture is dialysed until the free acid and the sodium chloride have been removed, there remains in the dialyser a perfectly clear colourless sol of silicic acid. This sol, either spontaneously or on addition of electrolytes—carbonates or phosphates being

particularly effective—sets to a bluish and almost transparent gel. No water separates, *i.e.,* the gel contains the same amount of water as the sol, and the transformation is irreversible, that is, the gel cannot be dissolved again. The change is also, as far as can be ascertained, continuous : the viscosity of the sol increases steadily until it becomes immovable, this feature forming an important distinction between gel formation and the solidification of molten substances, which is discontinuous. Silicic acid sols and gels are supposed to have existed in considerable quantities at some geological periods, and various minerals, like agate and opal, probably owe their origin to such gels.

The organic emulsoids are very numerous and extremely important, including, as they do, most of the proteids, such as albumin, casein, gelatine ; a number of carbohydrates as starch, agar, the gums, cellulose and its various nitro- and acetyl-derivatives ; the soaps, etc. It is impossible within the limits of a short work to do more than to select a few typical substances, and to develop a few general points of view to which their extremely varied behaviour becomes referable.

Two of these may usefully be considered together, viz., gelatine and agar. The former is a proteid, while the latter is a mixture of carbohydrates, the most characteristic of which is d-galactan. Both gelatine and agar, when immersed in cold water imbibe large quantities and swell, until an equilibrium is attained. On heating, they dissolve to sols, the temperature necessary to effect this being $25°$—$35°$ for gelatine, according to the concentration, and about boiling point for agar. On cooling these sols set to jellies, the setting point for gelatine being a few degrees lower than the " melting point," whereas the agar sol can be cooled to about $35°$ before setting. The process is completely

reversible, but the gels have to be heated to original temperatures, to be transformed into sols again. Agar is thus a very striking example of the phenomenon of hysteresis, as the sol, once formed, does not gelatinise until cooled to about $35°$, whereas the gel is not re-transformed into sol unless raised to a temperature nearly $70°$ higher. A similar, but very much slighter, hysteresis, is noticeable in the case of gelatine. As in the case of silicic acid the transformation is quite continuous, that is (with the same reservation regarding the difficulty of measurements in the neighbourhood of the setting point) the viscosity increases continuously as temperature falls.

The viscosity of gelatine sols has been the subject of careful and important investigations, particularly by Garrett. These tend to show that a gelatine sol, unlike a homogeneous liquid, has not a definite constant viscosity at a given temperature, but that the viscosity varies with the velocity of shear, and alters with time if shearing, even at constant velocity, is continued. Without entering into details of these investigations, which still present many difficulties, it may be said that the behaviour of the sol is inexplicable, except on the assumption that it is a system of two fluid phases, or, in other words, that it consists of drops or globules having a high gelatine content, in a continuous phase which is a dilute solution. The process of sol formation on this assumption becomes an extension of the process of swelling by imbibition, accompanied by disintegration. While the system is thus, mechanically, one of two liquid phases, it must be emphasised that it differs from an emulsion of two insoluble phases by the facility with which the solvent may be shifted from one phase into the other.

CHAPTER VI.

AN entirely different behaviour is shown by the albumins, which are perhaps the most important among the emulsoids, and have received an amount of investigation commensurate with their importance. As their type neutral albumin prepared from white of egg may be taken. This is soluble in water at ordinary temperature, and does not form a gel either with increasing concentration or on cooling. On the other hand, it shows a phenomenon we have not so far encountered : it coagulates irreversibly on heating to about 60°. The temperature at which this change occurs may be altered by the addition of salts, and can—as has been shown by Pauli and Handowsky—be raised so much by the addition of a thiocyanate that the sol does not coagulate even at boiling point.

In close connection with this property of the albumin sol is its behaviour to salts in the cold. On the addition of salts in suitable concentrations the albumin sol becomes turbid, and the albumin finally settles out in flocculent masses. The coagulum, however, shows different characteristics with different salts, and these, if for the moment we consider only the cation, divide themselves into three groups. The salts of the alkalies and of magnesium produce coagulation or " salting out " only in great concentrations, and the process is *reversible—i.e.*, on dilution or removal of the salt the albumin again goes into solution. The salts of the alkaline earths salt out in similar concentration, but the precipitate becomes insoluble on standing even for a short

time; while, finally, the salts of the heavy metals salt out irreversibly even in low concentrations.

If we now consider, instead of a variety of salts with different cations, a series having the same cation but different anions, we become acquainted with a sequence of the greatest importance, which was first discovered by Hofmeister in his investigations on egg albumin, and is generally called after him. Some of his results are given in the following table, which shows the concentration in moles per litre of the sodium salts of various acids necessary to salt out the same albumin sol at 30°—40°.

Citrate	0·56
Tartrate	0·78
Sulphate	0·80
Acetate	1·69
Chloride	3·62
Nitrate	5·42
Chlorate	5·52
Iodide	{ Do not salt out in
Thiocyanate	saturated solution.

This series refers to the neutral albumin investigated by Hofmeister. A further very striking fact was shown by Pauli : the effect of the series is reversed in faintly acid sols, in which the iodide and thiocyanate have the greatest, and the citrates and tartrates the least action.

At first sight no explanation whatever of these features suggests itself. The obvious temptation is to look for a chemical action, and the order in which the acids follow one another—tribasic, dibasic and monobasic—gives some plausibility to that view. It becomes, however, quite untenable when we study the effect of the series on other emulsoids besides albumin, for instance, on substances as dissimilar chemically as gelatine and agar. As far as a comparison is possible this is

parallel with the effect on albumin. The addition of citrate or tartrate to a gelatine or an agar sol raises the setting point and produces a stiffer gel; the addition of an iodide or a thiocyanate lowers it and leads to the formation of gel of slighter consistence. With sufficient concentrations of thiocyanate a gelatine or agar sol may be entirely prevented from setting to a gel at ordinary temperature. The viscosity of the sols is affected in the same sense. The only general view which coordinates all these phenomena is this: they are all various manifestations of a change in the distribution of water between the two phases, and the salts of the Hofmeister series affect this distribution, and do so by altering the compressibility of water. The solution of most emulsoids proceeds with contraction—a point which we shall discuss in greater detail when dealing with gels—and the view, propounded and supported with a great deal of evidence by Freundlich, that the effect of the Hofmeister series is closely connected with changes in the compressibility of water, is therefore entirely rational.

The emulsoids described so far, namely gelatine and agar on one hand and albumin on the other, are of two different types as regards their behaviour at different temperatures. The first named set to gels, without separation of water, below certain temperatures, while the latter coagulates irreversibly above a certain limit. A very large number of emulsoids do not exhibit either of these characteristics: they neither form gels at low temperatures nor coagulate on heating. This class contains practically all the emulsoids in solvents other than water, and many substances which form sols with water, such as the gums, starch, etc. Another member of this group is casein, which is peculiar in being insoluble in water alone, but soluble in weak

solutions of alkali. The alkali-casein sols are in many ways very typical emulsoid sols : they show a very rapid increase of viscosity with falling temperature and increasing concentration, without either gel formation or heat coagulation. The effect of the Hofmeister series, as far as it has been examined, is the same as on other sols, and casein also shows slight contraction in solution.

A similar behaviour, that is an absence of discontinuity at either extreme of temperature, is shown by gum arabic and similar sols. Gum arabic can be "salted out" by great concentrations of sodium chloride or other salts, the whole effect being again obviously due to removal of water from one phase into the other.

Among the sols with continuous phases other than water the most interesting are undoubtedly the sols of cellulose and of its nitroderivatives, which have assumed great industrial importance in recent years, as the materials for the production of artificial silk, etc. As is well known, cellulose is dissolved by cupric oxide-ammonia solution, forming a typical emulsoid sol of very high viscosity, from which the cellulose can be precipitated as a coherent gel by neutralising the solvent with acid. Cellulose is also gradually dissolved by a 50% zinc chloride solution at about 60°, and this sol is characterised by an even higher viscosity than the cuprammonium sol. The nitro-celluloses—collodion- and gun-cotton—form sols with a whole series of solvents, such as glacial acetic acid, acetone, ether-alcohol, amyl acetate, etc., all of which show the typical emulsoid properties : very high, but inconstant, viscosities, and slight turbidity or opalescence. With one of these sols, the acetic acid collodion, we are already familiar as a material for making ultra-filters : these sols leave a coherent gel like mass when the acetic acid is removed by water. Many of the other nitro-cellulose sols leave co-

herent films on drying, the properties of which can be modified by various additions, such as castor oil or camphor.

No special reference has so far been made to the electrical condition of the emulsoids, but from what has been stated in regard to salting out and related phenomena it is obvious that there is a profound difference between the suspensoids and emulsoids in this respect. The electric properties of the latter are not nearly as unambiguous as those of the former, and are affected, or, indeed, determined almost entirely by the reaction of the dispersion medium—i.e., the concentration of H or HO ions. This point also has been investigated chiefly in connection with albumin sols, especially by Pauli and his pupils. He showed that albumin freed as far as possible from electrolytes by prolonged dialysis and by freezing and thawing did not travel in the electric field, i.e., was not charged. In the presence of small concentrations of acid it assumes a positive charge, and in the presence of alkali a strong negative one. The conditions, however, are much more complicated than in suspensoids, as chemical reactions between bodies as sensitive as albumin and the added electrolyte must be expected, while they are not at all probable in many suspensoids.

The optical behaviour and the ultra-microscopic appearance of the emulsoids require only passing reference. The sols are all either slightly turbid or at least opalescent and show a marked Tyndall cone. In the ultra-microscope they cannot generally be resolved, that is, they show no particles, but only diffused light. As, apart from possessing a minimum size, particles to be visible must differ either in colour or in refractive index from the dispersion medium, their absence is easily accounted for : the difference between the two phases—a concentrated

disperse and a dilute continuous phase—may conceivably be very slight.

While there is thus a fairly sharp demarcation between the suspensoids and the emulsoids, there is a very gradual transition from the latter to true solutions. We know a whole range of substances the colloidal character of which is less and less marked, appears only in certain solvents or at certain concentrations, and is often confined to one or the other characteristic of emulsoid sols. Among these semicolloids may be mentioned the soaps—*i.e.*, the oleates, stearates and palmitates of the alkalies. In dilute aqueous solution they show a slight lowering of the vapour tension, which decreases with increasing concentration and disappears entirely at about one mole (about 28% of sodium palmitate). At that concentration we have a typical emulsoid sol, which sets to a jelly on cooling and can be " salted out," as is, indeed, done industrially. In alcoholic solution, on the other hand, the soaps show normal raising of the boiling point and all characteristics of true solutions. Tannin behaves somewhat similarly : the aqueous solution is turbid, froths, does not diffuse through parchment and shows no lowering of the freezing point, whereas in glacial acetic acid it is in true solution.

The colloidal character is still less marked in some of the products of cleavage of albumin, for instance in the peptones. They diffuse slowly but appreciably and show perceptible lowering of the freezing point : the only properties which link them to the emulsoids are slight turbidity and the syrup consistence which they assume with increasing concentration.

The dyestuffs, finally, show every possible variety of behaviour. Many of them, like eosin and methylene blue, appear " optically empty " in the ultra-microscope, diffuse and lower the freezing

point normally. Others, like congo red or benzo-purpurin, do not diffuse and show particles. Others again have emulsoid character, like fuchsin, which in concentrated solutions forms membranes on the surface and can be " salted out " with concentrated sodium chloride. A very exhaustive investigation of fifty dyestuffs of the indicator class has recently been completed by Wolfgang Ostwald, from which it appears that in practically all cases either the base or the acid, if not the dye itself, shows particles or at least a cone in the ultra-microscope.

CHAPTER VII.

REFERENCE has already been made in the preceding chapter to the changes which sols like those of gelatine and agar undergo on cooling, or which takes place in silicic acid sol on standing or the addition of electrolytes. The sols in these conditions set to coherent gels without loss of water and notwithstanding the very large amount of the latter present in some of them—2% agar makes a very stiff gel—they possess some of the properties of solids. This very striking fact, which at first sight is inexplicable, becomes intelligible to some extent when we remember organic structures, like the stems of plants, which show considerable rigidity and elasticity although containing 80 to 90% of water; these qualities are due to the liquid being enclosed in cells and vessels. We are probably not straining the analogy too much when we assume, even without further evidence—of which there is a considerable amount—that the gels must have some structure of this kind, that is to say, the liquid must be enclosed in cells formed by a solid phase. We shall return to this important question after the discussion of a few typical cases.

The gels are generally divided into "elastic" and "rigid" gels, gelatine, agar, the nitrocellulose-gels belonging to the former class, while silicic acid gel is the chief representative of the latter. The terms are not strictly correct, as the silicic acid gel can be felt to vibrate when the vessel containing it is struck, and must therefore possess some degree of elasticity, but they are sufficiently descriptive to be,
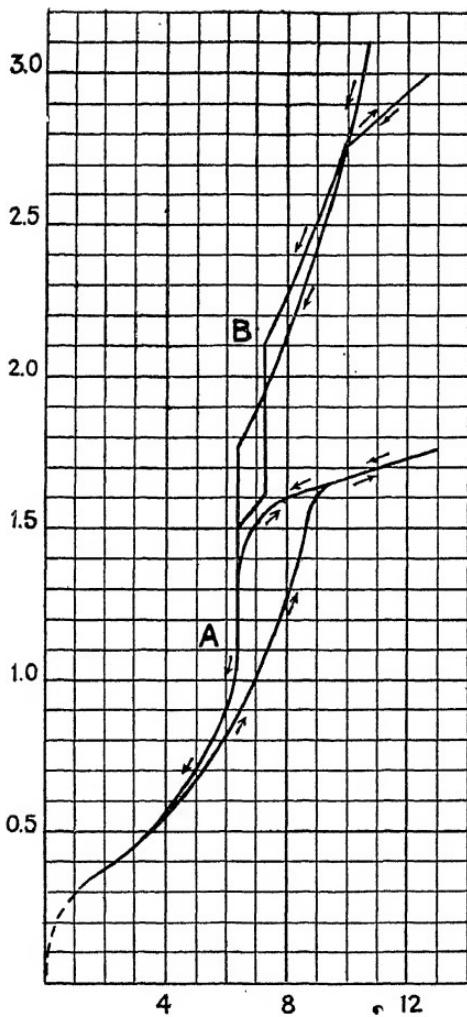
FIG. 9.

generally accepted. The silicic acid gel can be
obtained in its pure form by allowing a dialysed sol
to set (a process which can be very much accelerated

by bubbling carbon dioxide through it for a short time) and then forms an almost clear, faintly bluish jelly, containing up to 30 moles of water for one of SiO_2, *i.e.*, about 90% of the total weight of the gel.

If a slight excess of waterglass solution of about 1·16 sp. gr. is added to hydrochloric acid containing about 8% HCl, the mixture sets almost immediately to a white opaque gel, which of course contains the excess of sodium silicate and the sodium chloride formed by the reaction, but may nevertheless be used to demonstrate many of the properties of the gel.

The pure gel, if left in air, rapidly loses water even at ordinary temperature, but still retains several moles. These can be removed by drying over sulphuric acid, and the course of dehydration has been studied by van Bemmelen in a series of most exhaustive and careful experiments, prolonged in one instance for two years. The gels were kept in desiccators over sulphuric acid of known concentration and, therefore, vapour tension, and weighed at frequent intervals. The re-hydration was also investigated, and the complete results covering the range from 3 to 0 moles of water are plotted in Fig. 9 in which the abscissæ are the vapour tensions in mm. of mercury, and the ordinates the amount of water in moles.

The most important point brought out is that there are no definite hydrates, but that there is a continuous loss of water and an equilibrium corresponding to every given vapour tension. In this respect the gel differs radically from, say, crystals with water of crystallisation. Copper sulphate, *c.g.*, crystallises with 5 molecules of water : four of these are given off at 100° and the fifth at 200°. A dehydration curve plotted with the temperatures as abscissæ and the water contents as ordinates would therefore consist of two vertical lines—the process is discontinuous.

We meet here for the first time a class of compounds which are quite definite under given conditions, but in which the ratio of the constituents can change *continuously*, and not only by steps corresponding to simple stoichiometric ratios. Such compounds, known as " adsorption compounds," are of enormous importance in nature, and will be further considered in connection with the laws of adsorption.

The gel gradually undergoes a striking change in appearance during drying, which deserves mention, as it throws some light on the question of gel structure. At A the gel is still bluish and translucent, while at B it becomes chalky-white and opaque. On still further drying, however, it becomes clear again, and is almost transparent in the last part of the dehydration curve. We shall again refer to the probable meaning of these changes.

The elastic gels, like gelatine, have not been investigated in the same exhaustive manner, but ordinary experience already shows that their behaviour when taking up or losing water is entirely different from that of the rigid gel. Anyone familiar with photography, for instance, knows that the gelatine film does not become opaque at any stage of the imbibition or drying process. Another difference is noticeable in the behaviour of gelatine in water and in water vapour ; the amount of water taken up is not the same in both cases. Experiments on this point were made by Schroeder, who kept a gelatine plate, weighing dry 0·904 gramme, in air saturated with moisture for eight days, at the end of which it had taken up 0·37 gramme of water, the weight then remaining constant. The plate was then submerged in water at the same temperature and took up a further 5·63 grammes in one hour. If the gel is now placed into a dry atmosphere, it rapidly loses water at first—the speed

of evaporation being at first almost as great as from a free water surface—then very slowly, until an equilibrium depending on the vapour tension is finally reached.

This absorption of water by elastic gels, and the volume changes which accompany it, are of enormous importance physiologically, and have accordingly been much investigated, in the first instance by botanists. The following are the salient features of the phenomenon : when an elastic gel is placed in water, the gel imbibes some of it and swells, but the total volume gel plus water decreases, *i.e.*, the process is accompanied by compression. This can be shown in a variety of ways, of which the following, used by the author, is perhaps the most striking. One gramme of the gel to be examined is placed in an ordinary pycnometer, the latter filled with water and the whole weighed. The pycnometer is then placed under water, and left till the gel has swelled to the full extent, taken out, dried and weighed again. The excess represents the amount of water which has entered the pycnometer owing to the reduction of the combined volume gel plus water. In one experiment, in which 1 gr. of gum tragacanth was used, in a 50 c.c. pycnometer, the increase in weight after one week amounted to 0·9 grammes of water, *i.e.*, 0·9 c.c. of water had entered, or almost 2 % of the original volume. To obtain the same effect by compressing the water, a pressure of about 400 atmospheres would be necessary, and it follows at once that the process of swelling must be accompanied by the liberation of heat. This is, indeed, the case, and experiments have been made by many investigators to ascertain the amount of heat liberated during the swelling of gels. The following table gives the results obtained by Wiedemann and Luedeking, in gramme-calories per gramme of (dry) gel :—

Gel.	Gramme-Calories per gr. of gel.
Gelatine	5·7
Starch	6·6
Gum arabic	9·0
Gum tragacanth........	10·3

While the total volume gel plus water decreases, the gel plus *imbibed* water increases, *i.e.*, the gel swells. The increase in volume can of course be measured only by confining the gel in such a way that the water has access to it, but is not implicated in the volume changes ; for instance, by placing circular discs into a cylinder, which they fit exactly, and placing on top a weighted piston with numerous small perforations, through which water reaches the gel. Experiments with an apparatus of this description have been made by Reinke with the foliage of Laminaria, a seaweed, which behaves almost exactly like a gel. The table gives the pressure on the piston in atmospheres (kg. per sq. cm.) and the percentage increase in volume which the imbibition of water produces.

Pressure in Atm.	Percentage Increase of Volume.
41·2	16
31·2	23
21·2	35
11·2	89
7·2	97
3·2	205
1·2	318
1·0	330

This table also illustrates what large amounts of energy enter into the process. Even against the enormous pressure of over 42 atmospheres the gel still expands 16%, while with a pressure of 1 atmosphere the expansion amounts to 330%. In other words, 1 cubic centimetre of gel, if the swelling takes place in one dimension only (as in Reinke's

apparatus) will lift 1 kilogramme 3·3 cm. Conversely it becomes clear what enormous pressures are necessary to remove the last traces of water from a gel, as the present example still retains 16 % under a pressure of 42 atmospheres.

The various physical constants of gels—coefficient of thermal expansion, modulus of elasticity, the optical constants—are of great interest, as they differentiate the gels fairly sharply from both liquids and solids, but can only receive passing consideration here, as throwing light on their structure. If gels are not strained, they are isotropic, *i.e.*, they have the same coefficient of expansion, modulus of elasticity and refractive index in all directions. The coefficient of expansion in these circumstances is practically, and over a fair range, that of the liquid contained in the gel. If, however, a gelatine gel is stretched, it shows very remarkable anomalies ; on rapid warming it *contracts*, while rapid cooling produces *expansion*. It is worth noting that indiarubber, stretched beyond a certain limit, shows exactly the same behaviour, namely a *negative* coefficient of expansion, a fact which had already been observed by Tyndall.

As regards the elastic properties, the most important point is that gels are deformed without change of volume ; if, for instance, a gelatine cylinder is stretched, the cross section decreases in the same ratio in which the length increases, so that the product, *i.e.*, the volume, remains constant. Here, as in thermal expansion, the properties of the liquid portion of the gel are again seen to prevail.

Under stress, gels, which normally are isotropic, become doubly refracting, a property which they share with solids, such as glass. The change from simple to double refraction has been utilised to study their elastic properties, a subject into which it is not possible to enter here.

We have already touched on the question of gel structure at the beginning of the preceding chapter, where the view—based on a somewhat crude analogy—was expressed that gels were systems having a solid continuous phase, which enclosed or contained the liquid phase. It must be pointed out that the term "solid" is here—and, indeed, throughout our consideration of the whole subject —employed in a somewhat wider sense than is usual. It is intended to convey only that the phase to which it is applied is much less readily deformable than the liquid phase, without postulating all the properties, such as elasticity of shear, characteristic of a solid. The formation of reversible gels, like those of agar or gelatine, must therefore be accompanied by a change in the distribution of water, and we may naturally expect it to be affected by the presence of dissolved substances which modify this distribution, as explained in the chapter on emulsoids. This anticipation is found to be correct ; salts like the citrates or sulphates produce more rigid gels, while iodides or thiocyanates retard or prevent gel formation.

As regards direct evidence of structure in gels, a considerable amount of material has been collected by Bütschli, who examined and photographed numerous examples at very high magnifications, in some instances over 4,000 diameters. The photographs very generally show a structure, which is interpreted as resembling a honeycomb, *i.e.*, it appears to consist of polyhedral cells. Such cells were, for instance, visible in van Bemmelen's silicic acid gels while they were turbid, but disappeared at the stage at which the gel became transparent (see the preceding chapter). The explanation given by Bütschli is that the cell walls are so thin, compared with the wave length of light, as to be invisible until a film of water is formed on them by further hydration.

The interpretation of Bütschli's results has, however, always offered great difficulties into which t is not possible to enter here, but which are inherent n the formation of microscopic images of periodic structures whose order of magnitude is that of the wave length of light. More recent investigations with the aid of the ultra-microscope, carried out by Zsigmondy and by Bachmann, appear to show that the honeycomb formation shown by Bütschli's photographs is not the ultimate structure of the gel, and that this latter is ultra- or even amicroscopic.

Nevertheless, the existence of a gel skeleton— that is, a continuous solid phase—can hardly be doubted, and is supported not only by the reasonings already referred to, but also largely by the phenomena of diffusion in gels. That dissolved substances diffused into or out of gels was known already to Thomas Graham, and is a fact familiar to every photographer, as the various processes of developing, fixing, toning, etc., are made possible only by the diffusion of the respective solutions into the gelatine gel containing the silver haloid. Graham found that sodium chloride diffused in gelatine with almost the same velocity as in water, but this has been shown to be the case only with fairly dilute gels. In concentrated gels the rate of diffusion is considerably slower than in liquids, and it can be varied by the addition of various substances to the gel. This has been shown particularly by Bechhold and Ziegler, who found that the addition of sodium sulphate, glucose, alcohol or glycerine retarded diffusion, while urea, iodides and chlorides accelerated it. These substances affect the distribution of water between the two phases, and therefore probably the relative volumes of the gel walls and the free liquid. It is probable that diffusion takes place almost exclusively in the latter, as appears from another experiment by Bechhold, in which a

gelatine gel containing sodium chloride was covered
with an aqueous solution of silver nitrate of equiva-
lent concentration. In these circumstances an
extremely thin layer of silver chloride is formed,
which yet prevents any further diffusion. It can
be shown that the gel skeleton remains unaltered,
and that the silver chloride, which is sufficient to
prevent further diffusion, is formed only in the
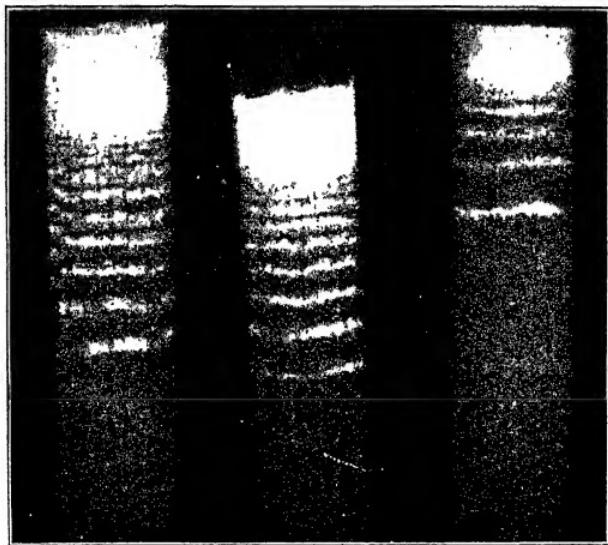
FIG. 10.

interstices, or in other words, that diffusion only
takes place in the latter, i.e., the liquid phase.

This experiment leads us to the consideration
of a further important section of our subject, that of
reactions in gels. If a gel contains a substance in
solution, and a second solution capable of reacting
with the former is allowed to diffuse into it, reaction
takes place, but exhibits a number of highly interest-
ing peculiarities. The most striking one is that, in
very many cases, the reaction does not proceed

ontinuously, but that the product is deposited in
trata separated by apparently clear intervals.
The phenomenon was discovered by R. E. Liese-
ang (after whom it is generally called) in the
ollowing manner : A drop of silver nitrate solution
vas placed on a film of gelatine gel containing
iotassium bichromate. The silver bichromate
vhich is formed by the reaction is not deposited in a
continuous zone round the drop, but in concentric
ings separated by apparently clear intervals. A
imilar structure is illustrated in Fig. 10 ; the test
ubes were partly filled with a 1% agar gel containing
calcium chloride, and on this were poured solutions
if sodium carbonate, the ratio of their concentra-
ions being 4 : 2 : 1. The calcium carbonate
ormed by the interaction is deposited in a number
if strata, and the effect of the different concentration
if sodium carbonate is strikingly shown.

No satisfactory explanation of these stratifica-
ions can be given at present, though a great number
if factors which may contribute to their formation
lave been pointed out by various observers.
This point is one which may be expected to receive
ncreased attention in the future.

Another feature of great interest has been
investigated chiefly by the present writer. By
choosing suitable concentrations of the gel itself,
and of the reacting salts, most of the insoluble
precipitates in the gel can be obtained in very large
crystals; in many cases, as with lead chloride,
lead sulphate, lead chromate, lead iodide, calcium
sulphate, barium silico-fluoride and others, they are
of macroscopic size. Many compounds also show a
marked tendency towards the formation of spherical
aggregates and perfect spherolites, giving the well-
known appearance between crossed Nicols, are
frequent. Figs. 11 and 12, for instance, show calcium
sulphate obtained in two different gelatine gels,

magnified 100 diameters. Calcium sulphate obtained by reaction in aqueous solutions of similar concentration forms fine needles, which, on the same scale would appear 3 to 5 mm. long.

These results show that large aggregates of very insoluble substances can be formed by reactions in

FIG. 11.
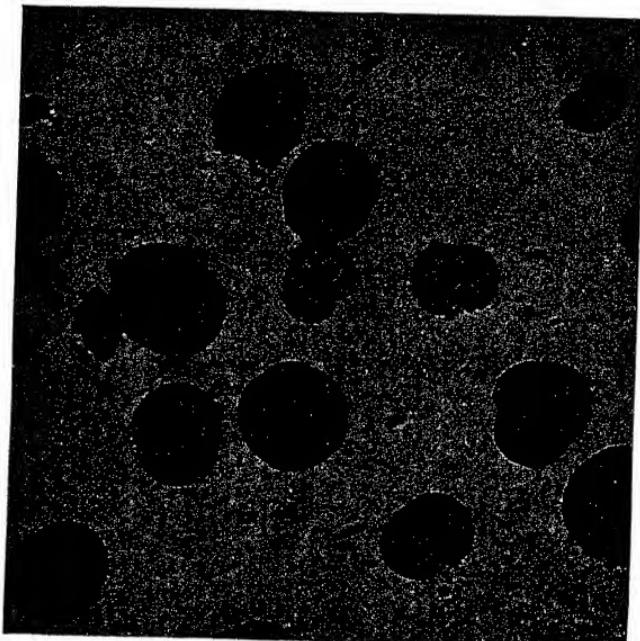
a gelatinous medium in comparatively short times; they thus throw considerable light on many questions of physiology, pathology and geology, detailed discussion of which, however, is beyond the scope of these articles.

The gels described so far are all formed by substances which are eminently colloids in Graham's sense, *i.e.*, bodies which have never been prepared

in a crystalline form.   Some cases are, however, known in which transient gels are formed by substances which crystallize quite well.   Several instances are known to organic chemists of reactions, in which a new phase first appears as a jelly, which

FIG. 12.

eventually breaks up and deposits crystals.   The author has examined two compounds of widely different constitution which show gel formation to a remarkable degree.   They consist of perfect crystals and are sparingly soluble in cold, more readily in hot, organic solvents.   On rapid cooling of the hot solutions no separation of crystals takes place, but they set to very perfect gels, which, however, are not stable.   After a shorter or longer

time they begin to liquefy and crystals of the substance appear. These transformations are of great theoretical interest, as possibly throwing light on gel formation in general, and explaining the formation of crystalline minerals from gels, but cannot be discussed in detail here.

CHAPTER VIII.

WE have already had occasion to emphasise the importance of the large boundary surface between the phases of a disperse system, inasmuch as it influences its electrical properties and, in the case of two liquid phases, its viscosity. We now have to consider a very large and very varied class of phenomena, in which this surface is the determining factor, all of which may be comprehensively described as changes of concentration in one phase at its boundary surface with another phase.

Many instances will be familiar to the reader, either from text-books or from actual use. Such are, for instance, the capacity of charcoal to condense large volumes of gases, of which advantage is taken for obtaining extremely high vacua. A similar property of charcoal, that of taking out of solutions colouring matter or the higher alcohols constituting "fusel oil," has been known since the end of the eighteenth century and is used industrially on a very large scale ; china clay and fuller's earth are also employed for purposes of the same kind. Another phenomenon of the same description is the power possessed by certain gels, such as gelatine and isinglass, of taking down turbidities in organic solutions. An instance familiar to the analyst is the well-known fact that the concentration of many solutions, *e.g.*, of lead salts, is considerably reduced by filtration through paper, that is, by contact with cellulose fibre.

This list could be extended very largely, but the instances given are sufficient to show that in all

cases the effect is produced at a boundary surface of considerable extent ; charcoal, clay, and even more strikingly the gels are all characterised by a very large surface development. Certain substances in solution are concentrated at these surfaces, and this change in concentration is now generally called adsorption.

The occurrence of these changes at surfaces also provides us with the clue to their investigation. We have already, when discussing emulsions, referred to the fact that the surface of a liquid against its own vapour, or against a second liquid, is in tension, known as surface tension in the former and as interfacial tension in the latter case. This tension is an extremely well-defined physical constant, and can be measured by a great number of methods. For details of these the reader must be referred to the text-books of physics or physical chemistry ; they all depend on the tendency of the surface tension to reduce the surface and to establish equilibrium with the other forces acting on the body of liquid under examination. As it takes work to produce or to enlarge a surface, it is, when formed, the seat of energy, which is measured by the product of surface and surface tension per unit length, and which, of course, tends to become a minimum. We already know of one way in which this may be accomplished, viz., by the surface becoming a minimum ; thus a drop of liquid suspended in another of the same specific gravity assumes spherical shape, the sphere having the minimum surface for a given volume. Obviously this is possible only where both phases are easily deformable, i.e., when both are liquid, or one liquid and the other gas.

The question now arises, whether such tensions and energies also exist at the surfaces gas-solid and liquid-solid, especially in view of the instances

quoted above, all of which refer to such systems.
It is obvious that the immediate methods of
demonstrating and measuring such tensions, as
applied to easily deformed phases, fail, since the
surface of the solid is not easily altered and does
not adjust itself to the tension. We can therefore
only conclude by various inferences, which cannot
be gone into here, that such tensions do actually
exist, and the evidence on this point is quite con-
clusive. The question then arises, whether the sur-
face energy at the boundary of a solid is a constant
for a given system, or whether by some means it
can assume a minimum value. Since it is the
product of the surface tension into the surface,
it can, of course, be reduced by reducing either
factor; in the case of a solid the second one, the
surface, is fixed, and any reduction which may occur
must be due to a decrease in the first factor, the
surface tension. It is at least a reasonable assump-
tion that *a change in concentration at the boundary
surface may be accompanied by such a reduction;*
if this assumption is correct, such a change ought to
take place, and this is what actually happens.

We have thus come to the conclusion that,
if in a two-phase system a change in the concentra-
tion of the liquid or gaseous phase will lead to a
decrease of surface energy, this change will occur;
to prove this view we have to investigate whether
in all cases where such changes appear there is a
diminution of surface energy. A change of concen-
tration can occur in a gas, if it is compressed at the
boundary surface, or in a solution, if the dissolved
substance is accumulated at the surface. Now we
know that charcoal, for instance, does condense
gases on its surface, or takes colouring matter out
of solution, but, as already pointed out, we have
no means of measuring the surface tension. We
must accordingly get evidence by studying similar

5—2

phenomena under conditions which permit such measurements, and this is possible by investigating the behaviour of a mercury surface against gases. The subjoined table gives the surface tension of mercury against vacuum (*i.e.*, its own vapour only) and various gases, one value being taken immediately after formation of the surface, the other after one hour.

Atmosphere	σ (fresh surface)	σ (after one hour)
Vacuum (15°)	436	436
Hydrogen (21°)	470	434
Oxygen (25°) ..	478	432
Nitrogen (16°) ..	489	438
Carbon Dioxide (19°) ..	480	436
Dry Air (17°) ..	476	429
Moist Air (17°) ..	481	429

It will be seen that the two values measured in vacuo are the same, that is, no change has taken place after one hour. In all the gases, however, the final value of the surface tension is considerably lower than the initial one, and this change is accompanied by the condensation of gas on the mercury surface. The rate of change is characteristic for each gas, and curves plotted with the times and tensions as co-ordinates agree very well with corresponding concentration-time curves obtained in the case of solid adsorbent materials. As the decrease in the surface tension mercury-gas is accompanied by compression of the latter, we must at once conclude that the surface tension of mercury should be lowered with rising gas pressure—a conclusion which has been experimentally verified.

The case discussed furnishes us with an instance in which the concentration—or, in other words, the pressure—of a gas has been altered at the surface of a liquid, with a change in surface energy, and we conclude that the same conditions hold good at

the boundary solid-gas. We may now consider an instance of the surface liquid-gas, in which the change of concentration takes place in the *liquid* phase, with the object of once more verifying that it is accompanied by a reduction of surface tension. We already are familiar with one simple criterion of lowered surface tension : froth formation. If we therefore take a solution exhibiting this characteristic and produce the largest possible surface, by making a froth, the latter ought to contain the dissolved substance in greater concentration. This reasoning has also been verified experimentally by various observers, especially by Miss Benson in the case of solutions of amyl alcohol in water, which froth copiously. Air is drawn through the solution, which carries the froth formed over into a second vessel ; the latter and the bulk are then analysed separately.

An excess of about $5\frac{1}{2}\%$ of alcohol is found in the froth, which result again confirms our reasoning.

We have thus some direct evidence to support the view that the changes of concentration, classed together as adsorption, on a surface are due to the tendency of the surface energy to attain a minimum value, and that they occur if an *increased concentration leads to a reduced surface tension*. Our whole knowledge of the matter, however, is not based exclusively on such reasoning, which, as far as the solid surface is concerned, rests on the uncertain ground of analogy, but the principal proposition has been proved by thermodynamical methods by Villard Gibbs. He arrived at the following famous formula :—

$$U = - \frac{C}{RT} \frac{d\sigma}{dC}$$

in which the symbols mean :

U excess of substance in surface layer

C concentration in bulk of liquid
σ surface tension
R the gas constant
T the absolute temperature.

The formula contains the differential coefficient of the function connecting surface tension and concentration, which is, of course, positive if both change in the same sense, and negative if they change in opposite senses. This, in conjunction with the minus sign on the right hand of the equation, shows at once that there will be a negative excess, *i.e.*, a diminished concentration in the surface, if the surface tension *increases* with increasing concentration, and a positive excess, *i.e.*, increased concentration in the surface, if the surface tension *decreases* with increasing concentration. The latter is the more common case, and confirms the results previously arrived at ; the former, however, has also been experimentally observed, and is known as *negative adsorption*.

CHAPTER IX.

FURTHER conclusions can be drawn from the formula. As the absolute temperature appears in the denominator, the excess in the surface, or, in other words, the amount adsorbed—whether positive or negative—varies inversely with the temperature, and decreases as the latter rises. It also follows that a *small* amount of dissolved substance can *lower the surface tension greatly,* but can only *increase it slightly.*

This somewhat surprising statement becomes intelligible when we remember that surface tension manifests itself only in the surface layer and depends on the composition of the latter. If a dissolved substance in increasing concentration increases the surface tension, the formula tells us that its concentration in the surface layer is less than in the bulk of the liquid, and its effect is thus counteracted to some extent. On the other hand, if in increased concentration it reduces the surface tension, it accumulates in the surface layer, thus enhancing its effect. As a matter of experience, minute amounts of accidental impurities often reduce the observed values of surface tensions considerably, while increases owing to small amounts of unintentional admixtures are not met with.

When more than one substance is present in a solution, the process becomes necessarily complicated, but one or two points may be discussed briefly. It is quite possible that the various substances may not be adsorbed to the same extent, in which case one or the other may be removed selec-

tively, as, *e.g.*, the colouring matter from sugar solutions. Where a single compound is dissolved in a dissociating solvent, the ions may likewise not be adsorbed equally, and the solution, originally neutral, may be acid or alkaline after adsorption ; this also has been found to be the case for instance, in van Bemmelen's experiments on the adsorption of potassium sulphate by gels, when the remaining solution was found acid, *i.e.*, the $K^{\cdot}$ ion was adsorbed to a greater extent than the SO_4'' ion. '

Although the formula does not include this term, it is obvious that the amount adsorbed, other things being equal, is proportional to the active surface— all substances, indeed, which are employed as adsorbents have very large surfaces. Charcoal retains the cellular structure of the raw material ; kieselguhr consists of very fine and extremely complicated siliceous, skeletons of diatoms, while the gels, as we know also possess a network or cellular structure with enormous surface. A material which has recently come into some prominence, especially through the work of Wislicenus, is the substance called in German " gewachsene Tonerde," *i.e.*, " grown alumina." This is an aluminium hydroxide, obtained by the oxidation of aluminium in presence of moisture and of extremely small quantities of mercury. It has a typical gel structure, and that its adsorbent effect is due to the latter is shown by the action remaining unaltered when the substance is dehydrated at red heat.

While we have thus a number of qualitative data regarding the phenomenon, one question is still open : whether it proceeds to any definite end point or equilibrium, and, if so, in what terms this can be expressed mathematically. These points are now settled by an enormous amount of material collected by various observers. One of the first experiments dealing with this problem was made by Wilhelm

Ostwald, who placed a quantity of charcoal in dilute hydrochloric acid, and after a certain time determined the concentration of the latter. If then a portion of either the charcoal or of the acid was removed, no further change took place, which tends to show that an equilibrium between the concentrations—on the surface and in the bulk of the acid—has been attained. Further decisive experiments are due to Freundlich, who placed charcoal in solutions of acetic and of benzoic acids of known strengths and determined the amount adsorbed. The same amounts of charcoal were then placed into half the volumes of acid of double the strength used in the first experiments and after a time an equal volume of solvent was added, bringing the total volumes to those used in the first instance. If there is a definite equilibrium between the adsorbed quantities and the end concentrations, the final concentration in the second experiment should be the same as in the first, and Freundlich in fact found this to be the case.

Mathematical investigation confirmed by an enormous amount of experimental work with a variety of adsorbents, solvents, and dissolved substances has established a definite relation between the quantity of adsorbent m, the quantity adsorbed y, and the end or equilibrium concentration c in the liquid after adsorption, which takes the following form :—

$$\frac{y}{m} = ac^{\frac{1}{n}}$$

in which a and n are constants depending on the nature of the solutions and the adsorbent. The curve corresponding to the above equation is known as the "adsorption isotherm," and it is obvious that it is a parabolic curve ; for $n = 2$, it actually becomes the ordinary conic parabola.

It may be pointed out here that the formula is very frequently, but quite erroneously, spoken of as an " exponential " one. An exponential expression is one containing one of the variables—in the present case these are y and c—as exponent, whereas the exponent in the equation of the adsorption isotherm is a constant. It is an interesting fact that this constant varies within comparatively narrow limits for the most widely different substances, viz., roughly speaking, between $n = 2$ and $n = 10$.

The principal deduction from the equation is obvious : the amount adsorbed, other things being constant, increases much more slowly than the concentration of the solution. This becomes quite clear by choosing a simple example in figures, say $n = 2$, and m and $a = 1$ (a simplification always admissible in any one series of experiments). In this case

$$y = c^{\frac{1}{2}}, \text{ or, in a more familiar form, } y = \sqrt{c}.$$

If we therefore take c, the end or equilibrium concentration successively equal to 1, 4, 9, 16, we find the adsorbed amounts to be the square roots of these numbers, *i.e.*, 1, 2, 3, 4. This means that, if double or treble the amount of substance is to be adsorbed, the remaining solution must be four or nine times as concentrated as for unit adsorption. As the initial concentration of each solution, before adsorption, is evidently $y + c$, we find that the initial concentrations corresponding to the adsorbed amounts chosen must be 2, 6, 12 and 20. Accordingly, in the example chosen, the initial concentration must be increased ten times if the adsorbed amount is to be four times as great.

The adsorption isotherms and the exponents $\frac{1}{n}$ have been determined for many substances and solvents. The table below shows a number of determinations by Freundlich.

Adsorbent.			Solvent.	Substance Dissolved.	$\frac{1}{n}$
Blood charcoal		..	Water	Formic acid ..	0·451
,,	,,	..	,,	Acetic acid ..	0·425
,,	,,	..	,,	Benzoic acid ..	0·338
,,	,,	..	,,	Picric acid ..	0·240
,,	,,	..	,,	Chlorine ..	0·297
,,	,,	..	,,	Bromine ..	0·340
,,	,,	..	Benzol	Benzoic acid ..	0·416
,,	,,	..	,,	Picric acid ..	0·302
,,	,,	..	Water	Patent Blue ..	0·190
Wool	..	..	,,	Patent Blue ..	0·159
Silk	..	..	,,	Patent Blue ..	0·163

The table shows clearly the limits between which the exponent varies, and a further point of interest is raised by the behaviour of the same solution— Patent Blue in water—towards three adsorbents as different as charcoal, wool, and silk. The value of the exponent does not differ greatly in the three cases, and it has been very generally observed that the influence of the adsorbent is very slight compared with that of the other factors. Various adsorbents have been investigated, but no quantitative relation has been established, and the difficulty of doing so becomes obvious when we remember that we have no means of determining and comparing the active surfaces of substances like charcoal and fibres. It is, however, fairly well established that the *order* in which various dissolved substances are adsorbed is the same for different adsorbents; if a substance A is more strongly adsorbed than another B, and the latter more than C, by charcoal, the same order will hold good for other adsorbing materials, although the numerical ratios may be altered.

Another question of importance has not been touched on so far, that is the effect of the solvent, in all cases where a substance is soluble in more than

one liquid. It is well known, even from general
experience, that the same substance is not adsorbed
equally out of solutions in different solvents, and
that adsorption is much slighter in organic solvents
than in water. Thus Freundlich gives the following
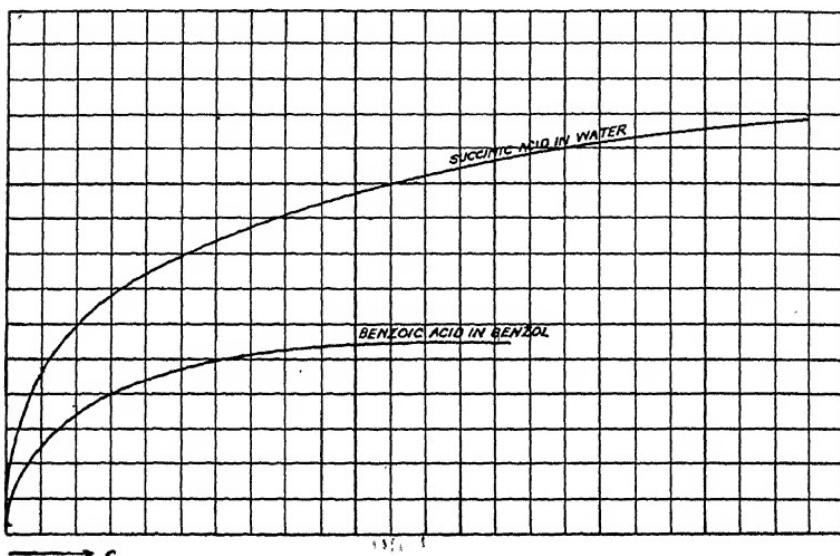
FIG. 13.—TYPICAL ADSORPTION ISOTHERMS.

figures for the adsorption of benzoic acid out of
solutions of equal strength in :—

Water	..	..	..	3·27
Benzol	..	..	..	0·54
Ether	..	..	..	0·30
Acetone	..	..	..	0·3

This peculiarity of organic solvents is practically
used for removing substances adsorbed out of
aqueous solutions. A dilute aqueous solution of a
dye, like crystal violet, can be completely de-
colourised by charcoal. If the latter is then placed

in alcohol, the adsorption from which is much lower, the surface concentration of the dye on the charcoal is in excess of that which would establish equilibrium, and a large amount of it therefore goes into solution.

Two typical adsorption isotherms are shown in Fig. 13. They are also due to Freundlich, and strikingly illustrate the parabolic character of the curve.

We are now in a position to explain, Freundlich's views of the precipitation of suspensoids by electrolytes, to which reference has been made. It will be remembered that trivalent ions act in much lower concentrations than divalent, and these again in lower concentrations than monovalent ions, but that the amounts actually found in the precipitate are equivalent. This means, that for each trivalent ion two divalent or three monovalent ions must be provided, as these amounts carry the same electrical charges. Freundlich suggests that the process, or at least the first step in it, is an adsorption. If the different ions are—as there is reason to believe—adsorbed at about equal rates, we can refer the process to one and the same adsorption isotherm for all three. By this means we can find the concentrations which are necessary to allow the corresponding amounts to be adsorbed. In other words, we draw three ordinates of the isotherm which are in the ratio 1: 2: 3, and the corresponding abscissæ give the concentrations. By doing this on one of the isotherms in Fig. 13, it will be seen at once how much greater the abscissæ becomes for the ordinate 2, representing the divalent ion, than for the ordinate 1, corresponding to the trivalent ion, and that the abscissæ of the ordinate 3, which represents the monovalent ion, is again very much larger than that of the ordinate 2.

The different rate of adsorption of substances present in a solution can be strikingly demonstrated,

and can be utilised for proving their presence in extremely minute quantities by allowing the solution to rise in long strips of filter paper. While this takes place, the dissolved substances are adsorbed by the fibre, so that beyond a certain height the liquid in the paper consists of pure solvent only. Different substances generally rise to different heights, and can be identified by their colour, or, if colourless, by appropriate reactions. The process can be demonstrated, for instance, with a very dilute solution of turmeric and picric acid, which is allowed to rise in a strip of filter paper about 12 ins. long. The strip is stained yellow, but if it is then exposed to ammonia, only the lower portion turns brown, showing that the turmeric has not risen as far as the picric acid. The method, which deserves to be more widely known than appears to be the case, may be used for showing the presence of colouring matter or preservatives in articles of consumption, and for many similar purposes. It has been developed— under the title of " Capillary analysis "—principally by F. Goppelsroeder, of Basle, who has demonstrated its extreme sensitiveness in favourable cases.

It is obvious that in all instances in which reactions take place in the presence, or lead to the formation, of finely divided solid matter, adsorption is possible, and may account for changes in concentration or losses. It offers thus a somewhat easy explanation of such phenomena, which, however, ought not to be taken as established without investigation, that is, measurements and the plotting of a curve, which must have the character of the adsorption isotherm, to establish this interpretation of what occurs. If the curve obtained is of a different type, it shows that adsorption, if it takes place at all, is accompanied by some other process. In this connection it should also be borne in mind that, even if chemical combination between the

adsorbent and the adsorbed substance is possible, the two processes need not occur simultaneously. This point is strikingly illustrated in an experiment by Bayliss, in which the blue Congo red acid— liberated from the dyestuff, which is a sodium salt, by acid—is adsorbed by aluminium hydroxide. The latter is stained *blue*, although all the salts of the acid are *red*, which shows that adsorption has taken place without chemical combination. The latter, however, occurs on warming, when the colour of the hydroxide changes from blue to red.

A process, which in a way may be looked upon as the converse of adsorption, is the extraction of a substance containing an admixture, with a solvent in which the latter only is soluble. It is evident that, if there is simply mechanical mixture, and if a sufficient quantity of solvent is employed, the whole of the soluble matter will be extracted by the first lot of solvent. It is equally obvious that this cannot be the case if the second substance is *adsorbed* by the first : in that event the first lot of solvent will, indeed, remove a large fraction of the soluble matter ; but as much of it as establishes equilibrium under the given conditions will be retained. A second lot of solvent will again remove a—much smaller— quantity, and so on. If a curve is plotted with the, preferably equal, volumes of solvent as abscissæ, and the amounts of soluble matter still retained as ordinates, curves of a hyperbolic type are obtained, and it is quite easy from these to construct the adsorption isotherm for the system under examina- tion, as will be clear from an actual example. Rubber, as is well known, contains varying amounts of " resin," *i.e.*, of substances soluble in acetone, and the results of extraction with successive equal portions of that solvent are shown in Fig. 14, taken from an investigation by D. Spence and J. H. Scott, published in the " *Kolloid-Zeitschrift*." The amounts

of resin still retained after each extraction are plotted as ordinates of the curve in full line at equal distances apart. It will be noticed at once that the first lot of solvent extracts a very large portion of the total resin contents, as shown by the
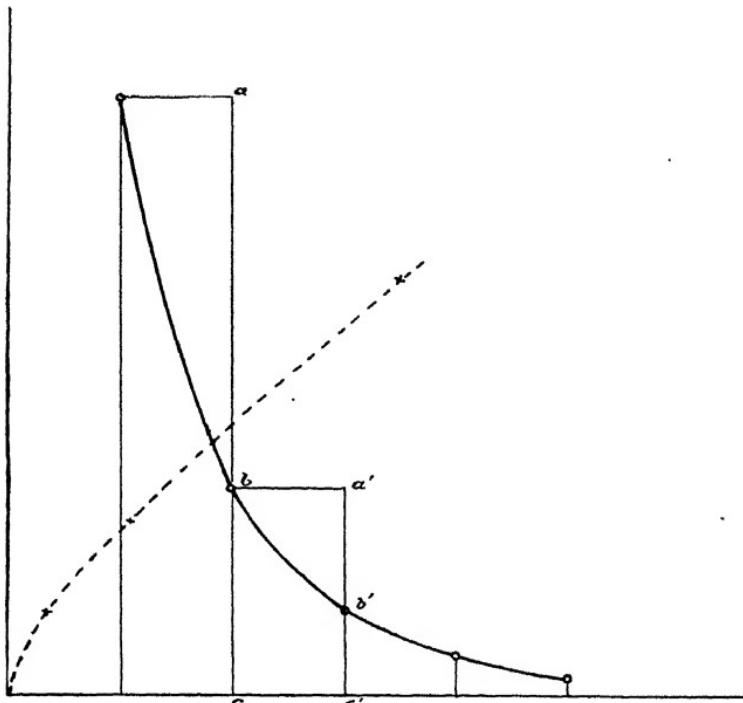

FIG. 14.

length *ab* on the ordinate *ac*. Similarly, the portion extracted by the second lot of acetone is given by the—much smaller—length *a'* *b'* on *a'* *c'*. The whole curve resembles a hyperbola, and it can easily be shown that the whole process is an inverted adsorption, both by analytical and by graphical methods. To adopt the latter, we consider the two portions of the ordinate *ac;* the part *ab* has gone into solution, while *bc* is retained by the rubber.

The latter therefore represents the amount adsorbed which is in equilibrium with the concentration in th solvent produced by dissolving the quantity ab If, accordingly, we plot the lengths $ab\ a'\ b'$, — — as abscissæ, and the lengths bc, $b'\ c'$— — as ordinate we obtain a curve which must have the character o the adsorption isotherm if the extracted matter i really retained by adsorption on the insoluble portion. This curve is plotted in dotted line, and i is obvious that it is of the familiar parabolic type.

(In the actual plotting of the dotted curve the ordinates have been doubled, to obtain a large scale.)

We have so far considered only phenomena in which the change in surface energy has been held to be the determining factor, and have disregarded th fact, with which we are already familiar, tha boundary surfaces are generally the seats of electri charges. It is more than probable that these may affect adsorption, and there are some striking phenomena in which the electric factors appear to play the most important or indeed an exclusive part If, for instance, a ferric hydroxide solution is passed through a column of sand—carefully purified—th hydroxide is completely retained, and only clea water leaves the end of the column for a time. Th same thing occurs with a solution of night blue, as ha been shown by Dreaper and Davis. In both case the sand is capable of retaining only a quite definit quantity : when this has been reached, the .iqui passes through unaltered. Both ferric hydroxid and night blue belong to the, not very numerous class of positive colloids, while silica, like mos substances, assumes a negative charge in contac with water. It is, therefore, reasonable to assum that the positive colloidal particles are discharge and retained by the negatively charged sand grain: Night blue is retained with such tenacity even by

smooth glass surface that vessels which have contained the solution cannot be washed clean with water alone. The phenomenon does not occur in an alcoholic solution of the dye, and, if the latter has been adsorbed on sand from an aqueous solution it can be removed by subsequent washing with alcohol.

It must be noted that the clear liquid which passes out of the column of sand is no longer, like the dye solution, neutral, but acid, *i.e.*, dissociation has taken place. The adsorption of highly dissociated substances is a subject to which passing reference has already been made, but our knowledge in this respect is still very incomplete. Cases of both positive and negative adsorption are known, and also numerous instances in which the anion and the cation are *not* adsorbed in equivalent quantities, that is, the solutions after adsorption show an excess of either, generally the anion. This, as already mentioned, is the case with potassium sulphate in van Bemmelen's experiments, also with salts of aniline and with many dyestuffs. The whole subject is in urgent need of much further investigation.

The general importance of adsorption hardly needs insisting on. Its connection with, and special importance in the study of colloids is also obvious ; since all the systems dealt with under this head possess very large surfaces, adsorption is an essential, if sometimes very obscure factor of the whole complex of phenomena to be observed. Thus adsorption undoubtedly takes place, not only in gels, but also on the surface of the disperse phase in sols. This has been proved directly, by means of conductivity measurements, by Wolfgang Ostwald, and by several other observers. Many authorities even hold that the electric charge on the particles is due to absorbed ions, and that the coagulation by

ectrolytes belongs to the same category, viz., is an
lsorption phenomenon.   Without going into the
etails of what are still highly controversial questions,
ference to them is necessary to remind the student
ıat adsorption is likely to play an important, if not
ıe determining, part in the formation and trans-
ırmations of all disperse systems.

CHAPTER X.

In the preceding chapters the reader has been furnished with a description—necessarily brief, but not omitting any feature of general importance—of the principal properties of disperse systems. It now becomes desirable to examine this whole mass of material with a view to finding, if possible, some general factors connecting the very various and striking phenomena.

We have been led to distinguish between systems in which the disperse phase consists of solid, or, more correctly, undeformable particles, and those in which the disperse as well as the continuous phase are liquid, that is, the disperse particles are deformable. In examining the former, we have found that there is a steady transition from suspensions to "suspensoids," due to the decreasing size of the particles and the consequent low velocity of settlement, increasing Brownian movement and increasing importance of the electric factors, which latter follows from the great increase of specific surface. The influence of the electric charge, although obscure both in its origin and its effect, on the stability of these systems has also received discussion.

In considering systems of two liquid phases, we have found that their chief mechanical difference from suspensions lies in the possibility of deforma·tion, which makes it possible to have any phase ratio. We found that this phase ratio, or rather a large volume of disperse phase with a small volume of continuous phase, is essential for the manifestation of high viscosity. These points refer both to

emulsions and to emulsoids, but a further peculiarity of the latter now deserves insisting on : the ready displacement of solvent from one phase into the other. We know that the disperse phase of the emulsoids consists of some form of aggregates containing large amounts of the solvent, and the striking changes in viscosity, and the sol-gel transformations under the influence of temperature, dissolved substances, etc., become referable to such a displacement of the solvent from one phase into the other.

In the emulsoid gels, such as silicic acid, gelatine and agar gel, we have finally become familiar with systems in which the continuous phase is solid—or, again to avoid certain difficulties—less deformable, and forms a skeleton or network filled with liquid. In these systems again the effect of surface becomes very marked, as some of their most characteristic elastic and optical properties are due to it.

We have finally studied in some detail the important phenomenon of adsorption or increased concentration on boundary surfaces. We have found that this occurs inevitably in all systems with large surfaces, and that it depends on two forms of energy inseparable from such surfaces, namely, electric and surface energy. Either of these factors may preponderate, or both may be active, in which case the phenomena become necessarily complicated, as in the case of dissociated substances.

It now remains to devote a few words to applications of colloidal science, both theoretical and practical. As regards the former, it can boast of one brilliant success: the study of the Brownian movement by Svedberg, Einstein, v. Smoluchowski and Perrin, which has afforded the most striking and convincing demonstration of the real existence of molecules. Less dazzling, but full of promise, are the numerous physiological investigations based on the properties of colloids which gradually tend to

elucidate how many fundamental phenomena, such as muscle contraction, become explicable as processes of water displacement due to alterations in the reaction of the tissue. The study of adsorption compounds is beginning to clear up a great number of debated questions in many different fields, such as the properties of arable soils at one end of the scale, and—what is one of the oldest and most famous debatable points in that branch of science— the nature of the latent image in the sensitive film of the photographic plate, at the other.

As regards the practical applications, it may perhaps be well to remind the reader, on one hand, of the youth of the whole discipline discussed here, and, on the other, of the twofold way in which the development of a new branch of science may bear on industries and arts. It may, of course, lead directly to new processes and manufactures : an instance is the production of squirted filaments of the refractory metals for incandescent lamps, which were made from the extremely finely divided metal coagulated from its sol. The much more general case—for which the growth of the chemical industries and of chemistry provides an illustration—is that it provides an explanation of phenomena long known and dealt with empirically. In this direction there is evidently a huge field for colloidal science, and the tilling—or at least the preliminary weeding and grubbing of the ground—may be said to be in vigorous progress. In all the industries which deal with organic raw materials, such as the textile and dyeing industries, brewing, tanning, the manufacture of explosive and other cellulose derivatives, to name only a few, there are numerous problems which have so far withstood solution by the methods of chemistry alone. For these the study of colloids provides, if not an answer at the first approach, at least an entirely new method of attack. It shows

us that the mere subdivision of matter, or, in other words, the production of large surfaces, brings into play energies, the effects of which may be of the most varied character, and of the most profound importance. It teaches, further, that these effects may again be modified extraordinarily by small alterations in the reaction of the medium, alterations which have no purely chemical explanation. It has familiarised us with the idea of adsorption compounds, *i.e.*, combinations in any ratio, but perfectly definite in certain circumstances of temperature and concentrations. It is, of course, for the investigator to apply all these considerations to his own problems, but he may be assured that there still is much room for them and him—not only, as the familiar phrase, which is meant to stimulate, but succeeds in depressing, has it "at the top," but even at the bottom among the foundations.

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